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13. ABSTRACT (Maximum 200 words)

This project emphasized the production of smart material systems using advanced 3-dimensional processing techniques. The specific aim was the fabrication and characterization of smart organic/inorganic composites at the mesoscale (~1nm - 1 mm length scale) to achieve improved performance. Two approaches were used: (i) the synthesis and processing of organic/inorganic composites and (ii) developing two novel materials systems. Synthesis and processing studies involve the use of three methods: (i) laser stereolithography, (ii) self-assembled monolayers, and (iii) 3-dimensional co-assembly. The two novel systems developed for use in sensor and actuator technologies were piezoelectric shell transducers and 1-3 piezocomposite hydrophones.

This is the final technical report for the project, covering period 06/19/1995 - 05/31/2001. Proof of concept and feasibility studies have successfully demonstrated (i) the utility of rapid prototyping in the fabrication of ceramic structures for use in sensor and actuator applications; (ii) the formation of mesostructured ceramics via templation of liquid crystal structures in solution; (iii) guided growth and orientation in microcontact printing microinfiltration; and (iv) optimization of piezo-composite properties through analytical modeling.

14. SUBJECT TERMS
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Smart Materials Systems through Mesoscale Patterning

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Scientific Progress and Accomplishments

The accomplishments for the project are detailed in the following sections. Active projects during the period of performance include the following task areas:

1. Piezoelectric Cantilevers as Sensors
   Wan Y. Shih, James S. Vartuli, David L. Milius, Huiming Gu, Xiaoping Li, Wei-Heng Shih, and Ilhan A. Aksay
2. Dynamics of Piezoelectric Cantilevers-Size Sensors
   Peter C. Y. Lee, Rui Huang, Ninghui Liu, and Arthur Ballato
3. Synthesis and Characterization of PMN-PT Piezoelectrics
   Huiming Gu, Wan Y. Shih, and Wei-Heng Shih
4. Stereolithography of Organic/Inorganic Composites
   Robert K. Prud'homme, Ilhan A. Aksay, David L. Milius, James S. Vartuli, Rajeev Garg, Aaron J. Dulgar, Peter J. Photos, Jim H. Lee, and James Liang
5. Mesoscopic Composites as Small Materials Systems
   George M. Whitesides, et al.
6. Micropatterning through Field-Assisted Flow
   Ilhan A. Aksay, George M. Whitesides, Sol M. Gruner, Robert K. Prud'homme, Dudley A. Saville, James S. Vartuli, Daniel M. Dabbs, Matt Trau, Srinivas Manne, Linbo Zhou, Anthony Ku, Hak Fei Poon, and Macit Ozenbas
7. The Sponge Phase: Synthesis and Characterization
   Sol M. Gruner, Karen J. Edler, Daniel M. Dabbs, Nan Yao, Aaron Rabinovitch, Akin Akinc, Robert K. Prud'homme, and Ilhan A. Aksay
8. L_3 "Sponge" Phase: Applications
   Daniel M. Dabbs, Sol M. Gruner, Karen J. Edler, Nan Yao, Aaron Rabinovitch, Akin Akinc, Robert K. Prud'homme, and Ilhan A. Aksay

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88. W. Happer, G. Cates, M.-F. Hsu, and I. A. Aksay, "Sol-Gel Coated Polarization Vessels," U.S. Provisional Patent Application Serial No. PCT/US98/16834; Docket No 98-1443-1.

89. R. K. Prud'homme, I. A. Aksay, and R. Garg, "Method for the Preparation of Ceramic Articles," U.S. Patent Application Serial No. 846,764; Docket No. 98-1470-1. (Co-owned by Dow Chemical Co.).

90. I.A. Aksay, R. Garg, R.K. Prud'homme, "Controlled Microarchitecture Ceramic by Stereolithography," U.S. Patent Application Serial No. 09/191,606, Docket No. 98-1500-1.

Invention Disclosures

91. J. S. Vartuli, , R. K. Prud'homme, W.-H. Shih, D. L. Milius, W. Y. Shih, X. Li and I. A. Aksay, "Multi-Layer Piezoelectric Laminate," Docket No. 98-1512-1.

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(Continuation Sheet)

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Macit Özenbaş, Middle East Technical University, Turkey

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REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Technology Transfer

Collaborations and Interactions

Army Research Office

ARO, U.S. Army Research Laboratory, Arthur Ballato, Fort Monmouth, New Jersey

Industrial

PrinDrex technology licensed to Leading Edge Ceramics

Sponge phase technology licensed to American Biomimetics

Ceramic stereolithography licensed to Johnson and Johnson

L_3 phase technology transfer agreement with Lucent Technologies

Other Industral Connections

Company/Corporation	**Contact**	**Company/Corporation**	**Contact**
3D Systems Valencia, California	Dr. Paul F. Jacobs	Johnson & Johnson Somerville, New Jersey	Dr. Mark Roller
Dow Chemical Co. Midland, Michigan	Dr. Alan M. Hart Dr. Alek J. Pyzik	Rohm and Haas Specialty Materials Spring House, PA	Dr. Edward Greer
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Lord Corporation Cary, North Carolina	Dr. Gerald Estes	Lucent Technologies Murray Hill, New Jersey	Dr. Cherry Murray Dr. Howard Katz
Allied Signal	Dr. Clifford Ballard	ILC Cherry Hill, New Jersey	Mr. Howard Stein
Leading Edge Ceramics Seattle, Washington	Mr. Clare Nordquist	Praxair Specialty Ceramics Seattle, Washington	Mr. Randy Kurosky
Nanodyne Piscataway, New Jersey	Mr. Frank Shinnemon	AMT Venture Partners Dallas, Texas	Mr. Tom Delimitros

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

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ROBERT K. PRUD'HOMME[§], WEI-H. SHIH[*], WAN Y. SHIH[*‡]
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FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

Department of Chemical Engineering and
Princeton Materials Institute
Princeton University

Smart Materials Systems through Mesoscale Patterning

Ilhan A. Aksay,[§] Sol M. Gruner,[†] Peter C. Y. Lee,[‡]
Robert K. Prud'homme,[§] Wei-H. Shih,[*]
Salvatore Torquato,[‡] and George M. Whitesides[#]

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Goals and Organization

PROCESSING TECHNIQUES

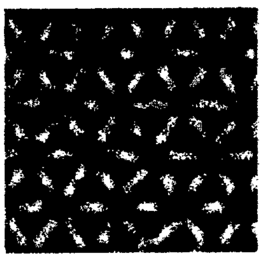
Self Assembly

(a) Amphiphilic and Protein Membranes

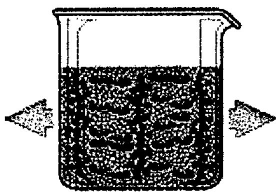
1 -10 nm

Groves, Hecht, Aksay (NSF)

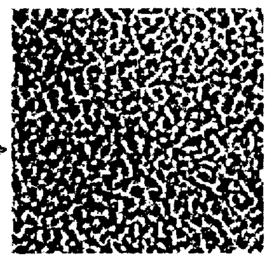
(b) Liquid Crystal Templating



Cubic phase



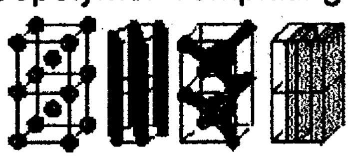
1 -10 nm



Sponge phase

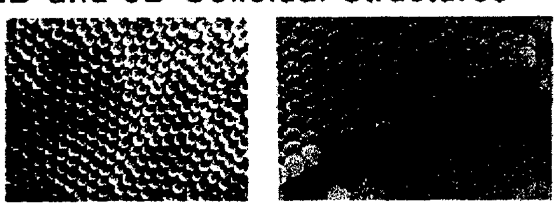
Dabbs, Saville, Aksay

(c) Block Copolymer Templating (NSF)



10 - 100 nm

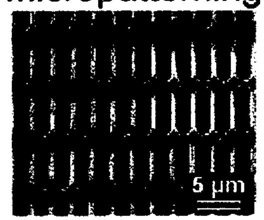
(d) 2D and 3D Colloidal Structures



Saville, Aksay

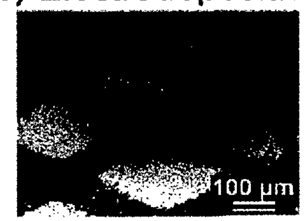
Laminating and Micropatterning by Field-Assisted Flow

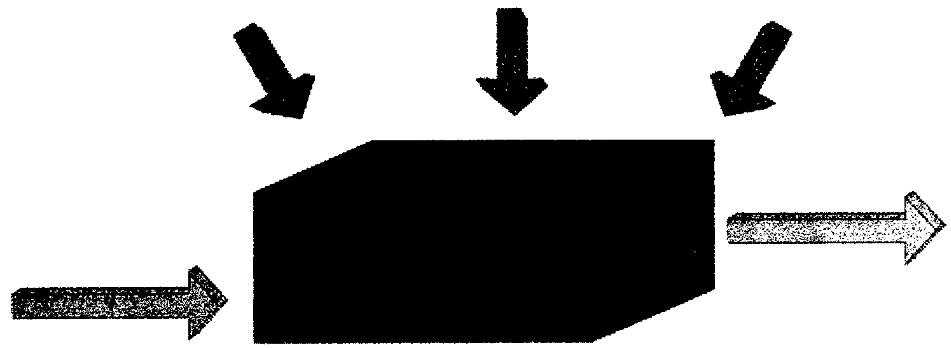
(a) Micropatterning



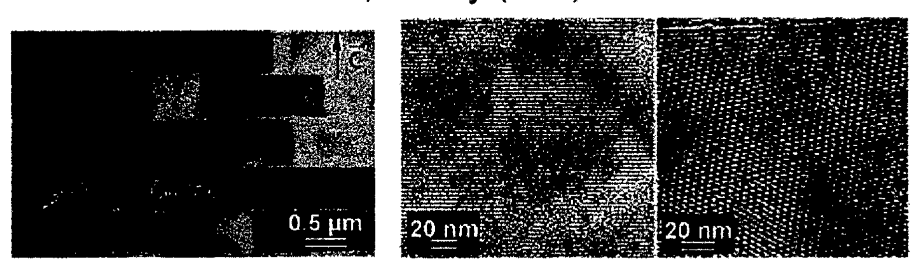
(b) Cone/Jet

(c) Electrodeposition



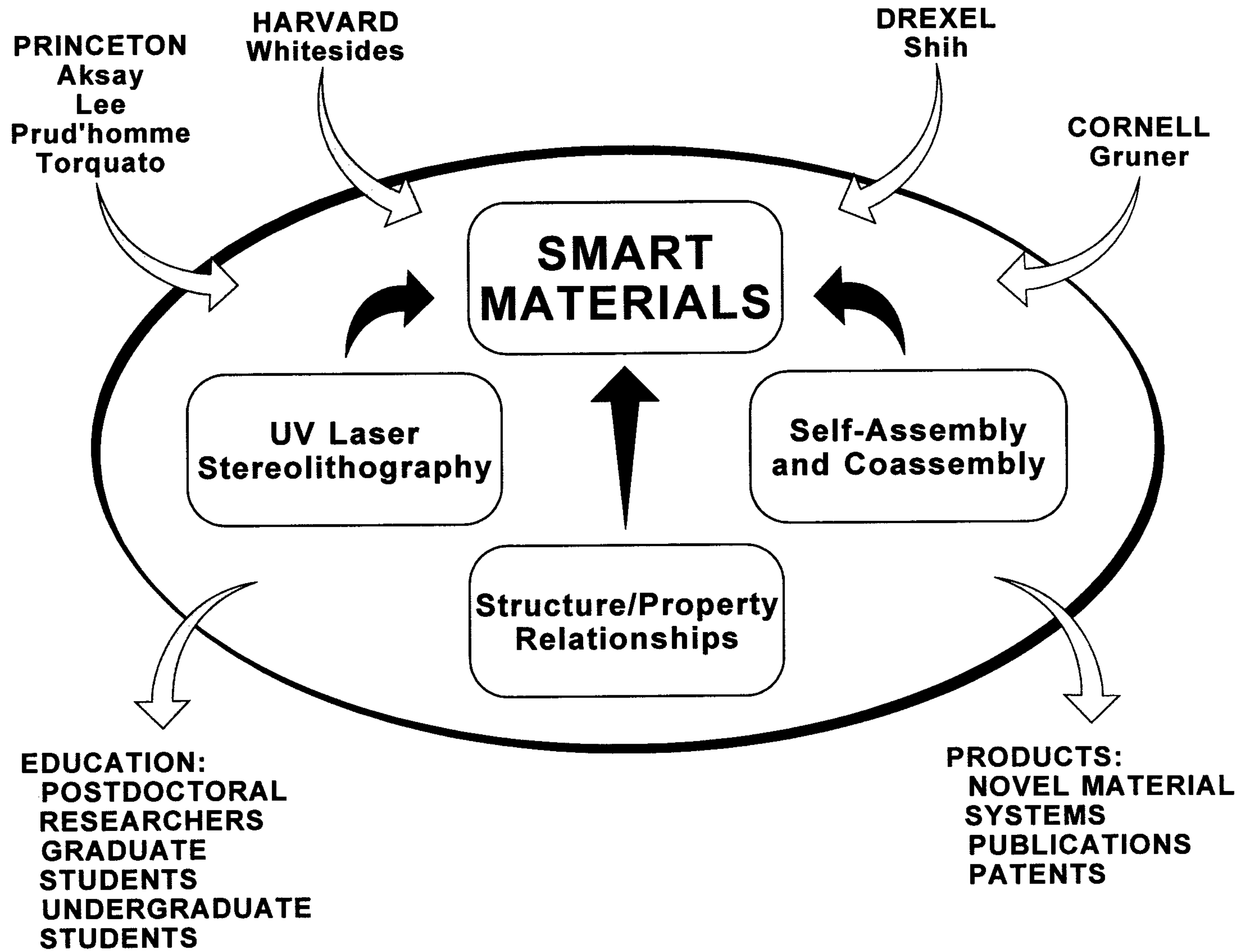


Hierarchically Structured
Nano- and Microlaminates
Suo, Evans, Soboyejo, Saville,
Groves, Aksay (NSF)



OPTIMAL PROPERTIES

Research Dynamics: We Kept Our Promise!



Organization of Research Teams

Principal Investigator: Ilhan A. Aksay

Ceramic and Polymer Processing

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- R. Wang

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- S. Rea
- K. LaMarche
- C. Brown
- J. McDonald
- D. Volk

Self-Assembly and Coassembly

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- H.-F. Poon
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SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Piezoelectric Cantilevers as Sensors

WAN Y. SHIH[§,#], JAMES S. VARTULI[§,#], DAVID L. MILIUS[§,#], HUIMING GU[‡], XIAOPING LI[‡], WEI-HENG SHIH[‡], AND ILHAN A. AKSAY[§,#]

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FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
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Piezoelectric Cantilevers as Sensors

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[*]Department of Materials Engineering, Drexel University

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Supported by the ARO/MURI under Grant No. DAAH04-95-1-0102

- ***Using cantilevers as microsensors in a wet environment, e.g., in a biological system***

- ***Detection of human viral pathogens, cholesterol, protein, etc. in blood supply and in blood stream***

  $\Rightarrow$ **In a liquid environment,** damping **is important**

  $\Rightarrow$ **How does the effect of damping changes as the dimension of the device shrinks?**

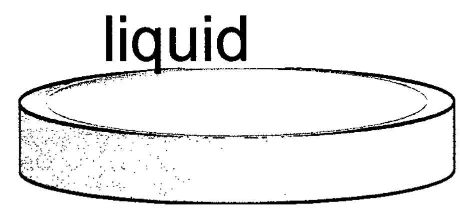
Existing viscosity sensors

- ***Using resonance-frequency change and/or peak broadening to deduce the liquid viscosity.***

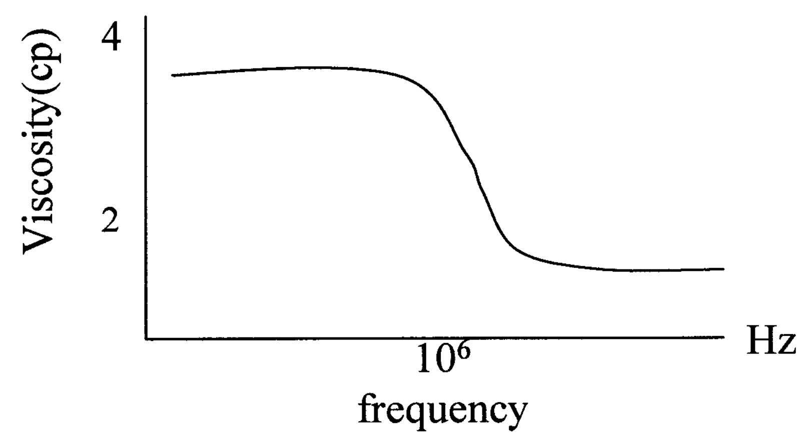
  (1) Thickness-mode sensors (1-50 MHz)

  Quartz membrane

  Ultrasonic viscosity sensors

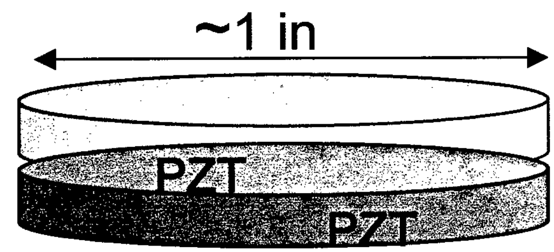


Disadvantages: **higher frequency viscosity depends on frequency**



(2) Flexural sensors:

(I) PZT-bimorph-disk oil viscosity sensors



Advantage:

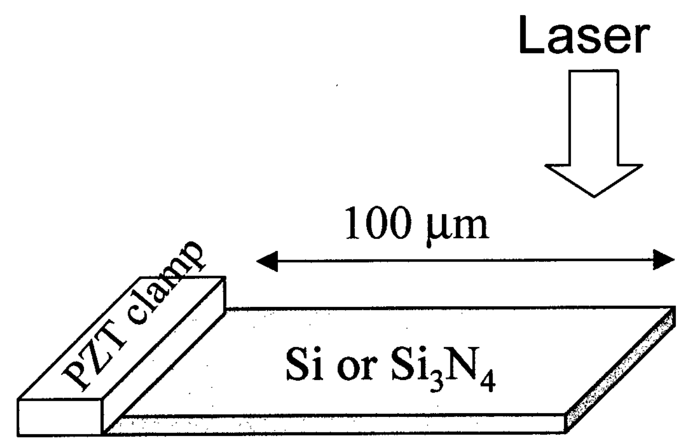
lower frequencies (kHz)

Disadvantage:

low sensitivity

frequency change ~ 2-3%

(II) silicon, silicon nitride microcantilever viscosity sensors



Advantages:

(i) lower frequencies (kHz)

(ii) higher sensitivity

frequency change ~ 100%

for viscosity change 1-200 cp

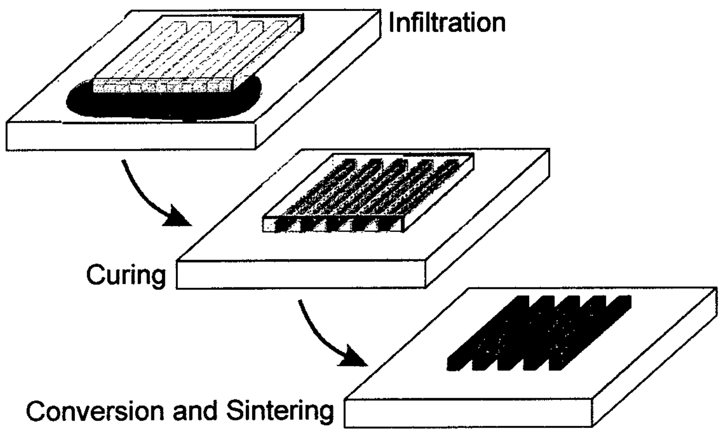
Disadvantage: (i) require a laser

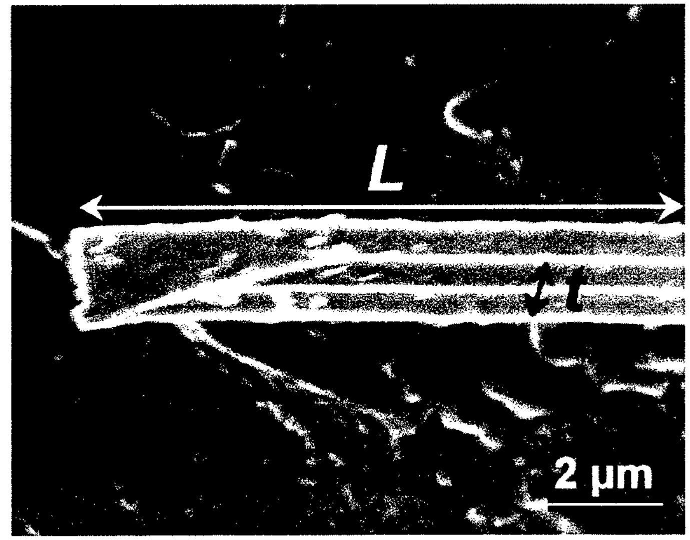
Objectives

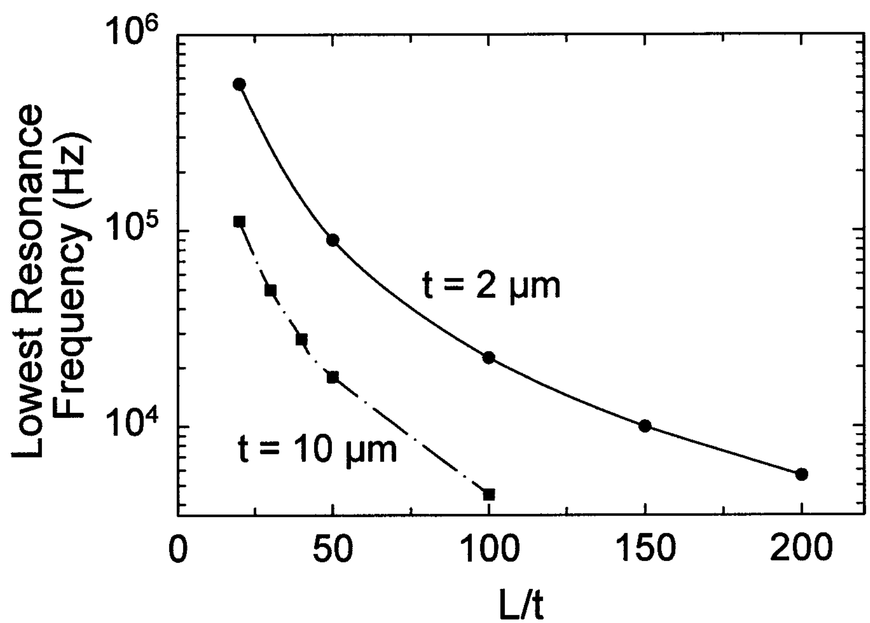
(1) To develop a viscosity sensor that

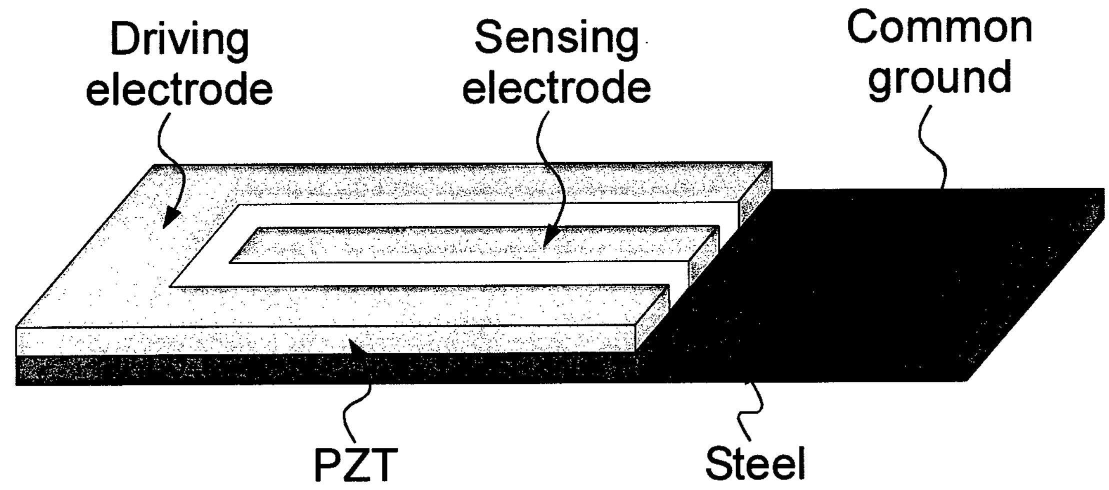
- operates at a low frequency
- easy and cheap to operate
- desirable sensitivity

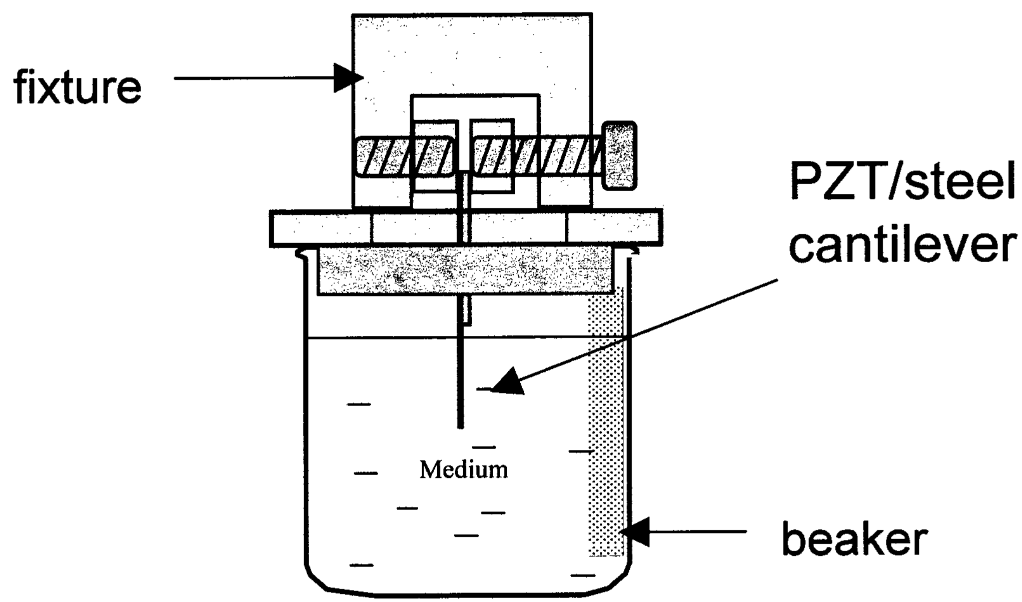
(2) To explore other sensing possibilities (e.g., material sensing) in a wet environment


Infiltration
Curing
Conversion and Sintering

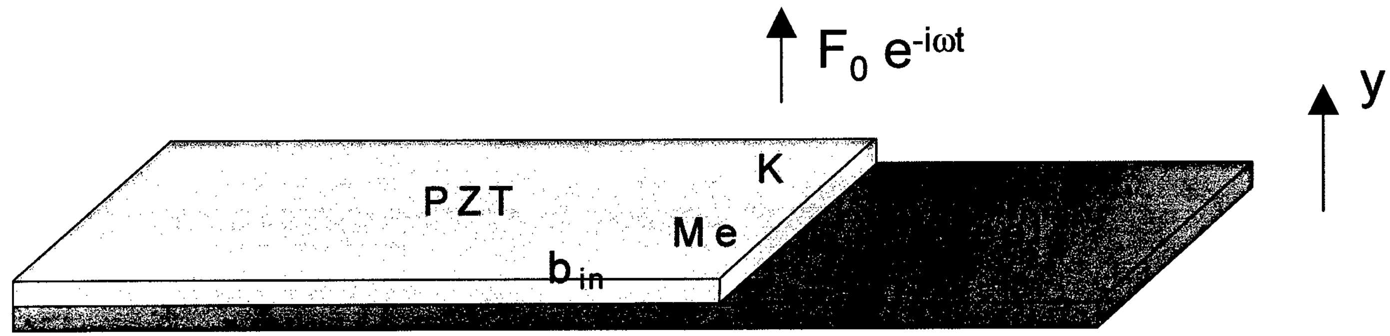

L
t
2 μm


Lowest Resonance Frequency (Hz)
10^6
10^5
10^4
t = 2 μm
t = 10 μm
0
50
100
150
200
L/t


Driving electrode
Sensing electrode
Common ground
PZT
Steel


fixture
PZT/steel cantilever
Medium
beaker

$$(Me + MI)\frac{d^2 y}{dt^2} + (b_{in} + b)\frac{dy}{dt} + Ky = F_0 e^{-i\omega t}$$



ω =angular frequency,

Me =effective mass at the tip of the cantilever

K =effective spring constant at the tip of the cantilever

MI =induced mass from the liquid

b =damping coefficient due to the viscous liquid,

b_{in} =the intrinsic damping coefficient of the cantilever.

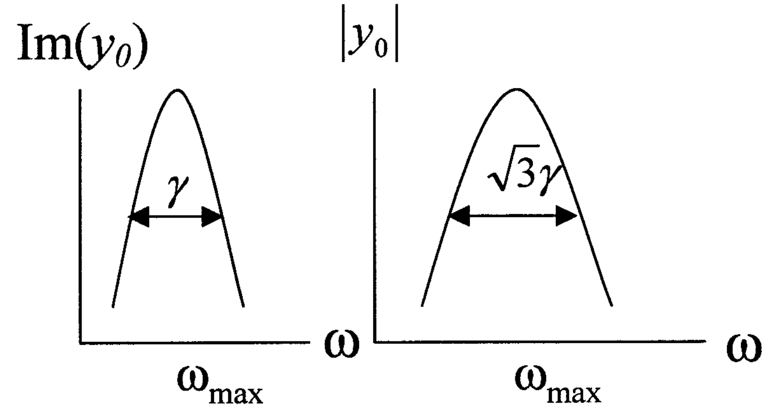
$$y = y_0 e^{-i\omega t} \qquad y_0 = \frac{-F_0}{\left(\omega^2 - \omega_0^2\right) + i\omega\gamma}$$

$y_{0,max}$ and $\mathrm{Im}(y_0)$ occurs at ω_{max}: $\quad \omega_{max}^2 = \omega_0^2 - \frac{1}{2}\gamma^2$

at $\omega = \omega_{max}$

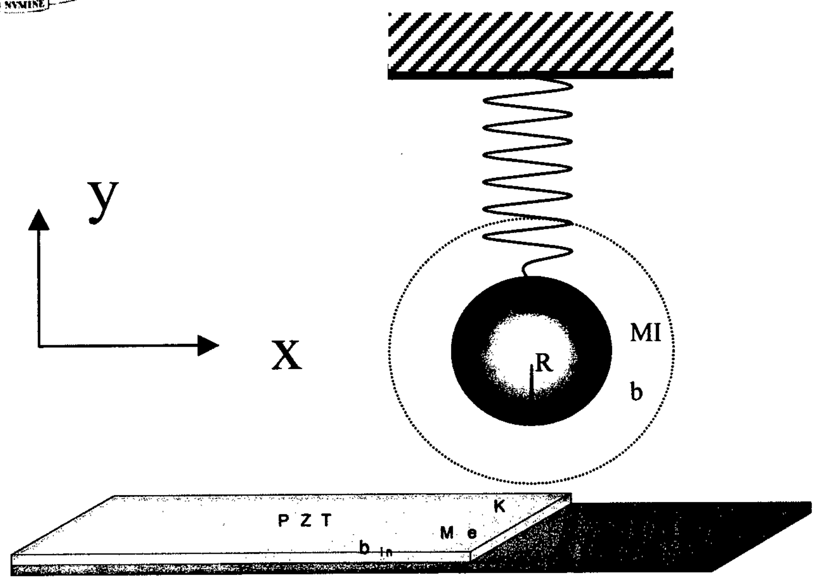
$$\left|y_0\right|_{max} = \frac{F_0}{\omega_{max}\gamma}$$

$$\mathrm{Im}(y_0)_{max} = \frac{F_0}{\omega_{max}\gamma}$$



$$\omega_0 = \sqrt{\frac{K}{Me + MI}}$$ = resonance frequency in liquid without damping

$$\gamma = \frac{b + b_{in}}{Me + MI}$$ = damping coefficient per unit mass



R = radius of oscillating sphere

$\rho =$ liquid density

$\eta =$ liquid viscosity

The induced mass

$$MI = \frac{2\pi R^3}{3}\rho\left(1+\frac{9}{4}\frac{\delta}{R}\right)$$

The damping factor

$$b = \frac{6\pi\eta R^2}{\delta}\left(1+\frac{\delta}{R}\right)$$

$\delta = \sqrt{\frac{2\eta}{\rho\omega}}$ = the decay length in the liquid

For $\omega=\infty$:

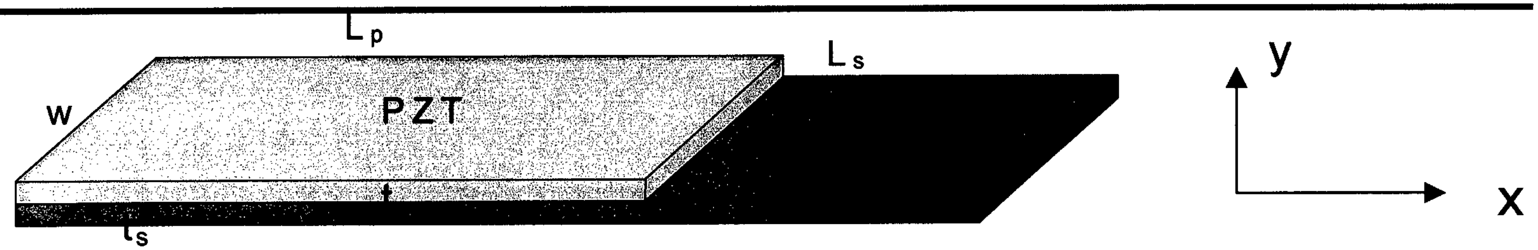
$$MI_\infty = \frac{2\pi R^3}{3}\rho$$

$$b_\infty = \frac{6\pi\eta R^2}{\delta}$$

For $\omega=0$:

$$MI_0 = \frac{3\pi R^2}{2}\delta\rho$$

$$b_0 = 6\pi\eta R$$



The spring constant at the end of the PZT plate (at $x = L_p$):

$$K = \frac{3D_P w}{L_p^3}$$

For the present cantilever, the effective mass

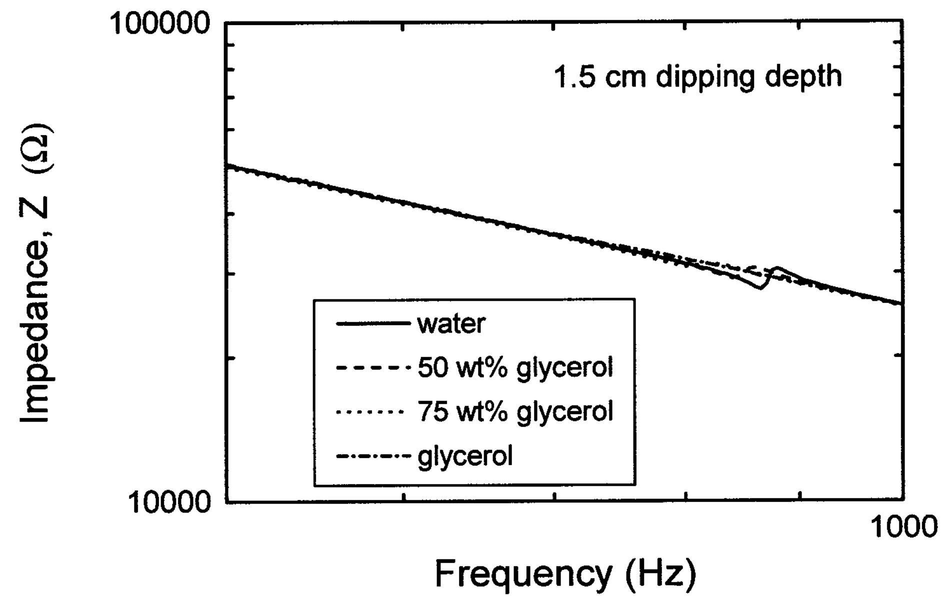
$$Me = 0.236(\rho_P h_P + \rho_s h_s)wL_p + \rho_s h_s wL_s$$

D_P = bending modulus of the PZT/steel

$$D_P = w\frac{E_p^2 h_p^4 + E_s^2 h_s^4 + 2E_p E_s h_p h_s(2h_p^2 + 2h_s^2 + 3h_p h_s)}{12(E_p h_p + E_s h_s)}$$

The lowest resonance frequency in air: $f_1 = \frac{1}{2\pi}\sqrt{\frac{K}{Me}}$

ρ_p, ρ_s = densities of PZT and steel
E_p, E_s = Young's moduli of PZT and steel



Impedance $$z = \frac{-i}{\omega c} + iz_i$$

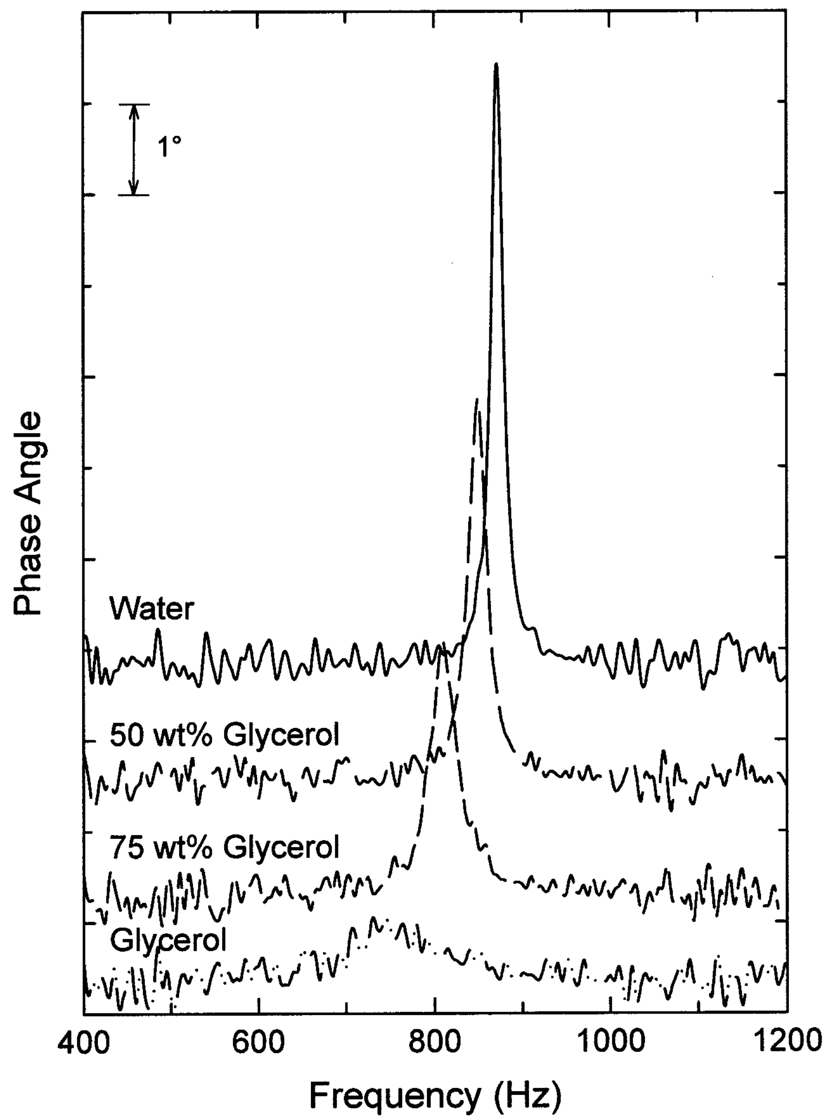
c = capacitance of unimorph

iz_i = induced impedance due to flexural displacement

$$c = 6.0\ \text{nF}$$

$$iz_i = \frac{i\alpha}{\left(\omega^2 - \omega_0^2\right) + i\omega\gamma}$$

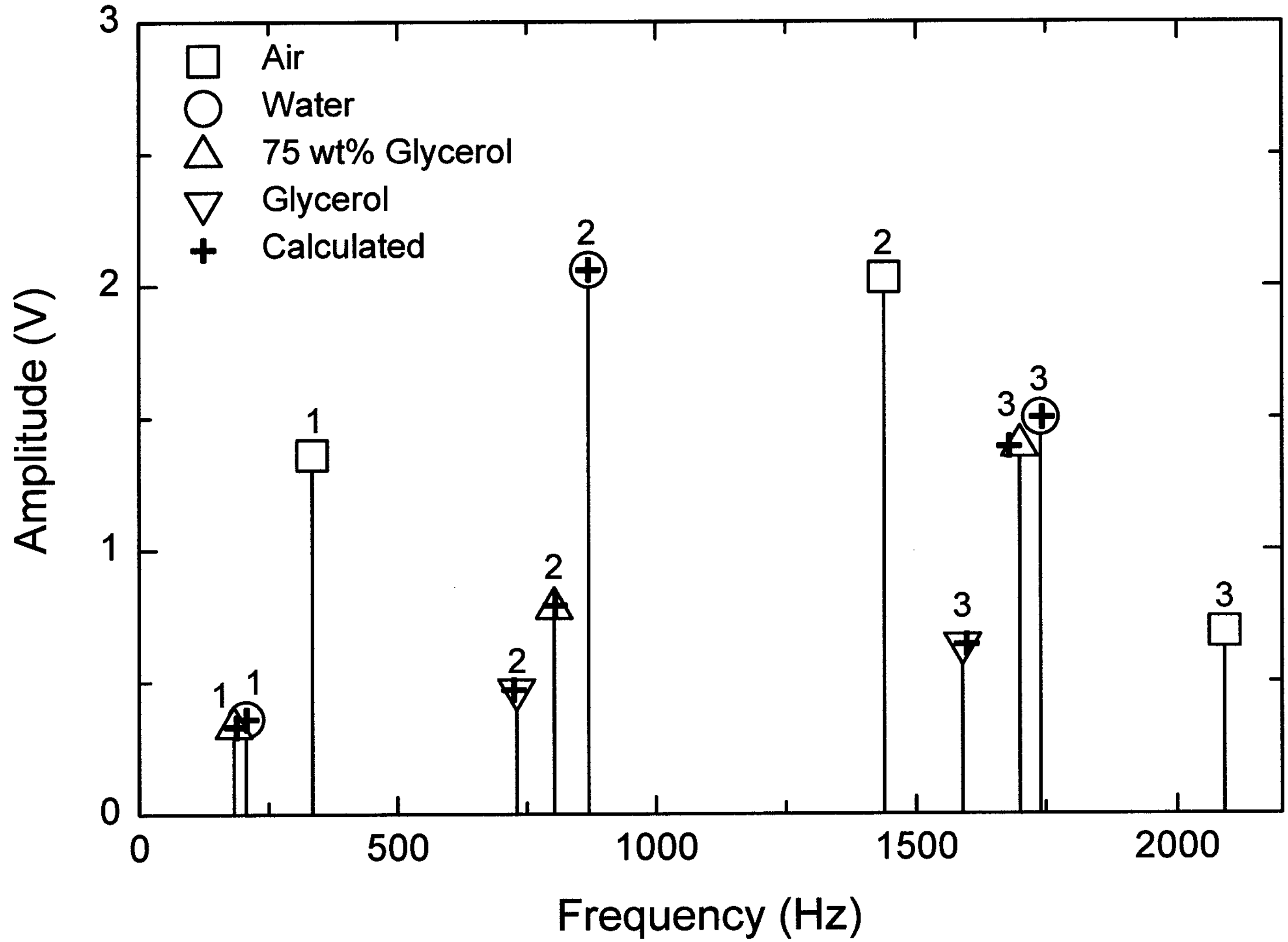
α = proportional constant

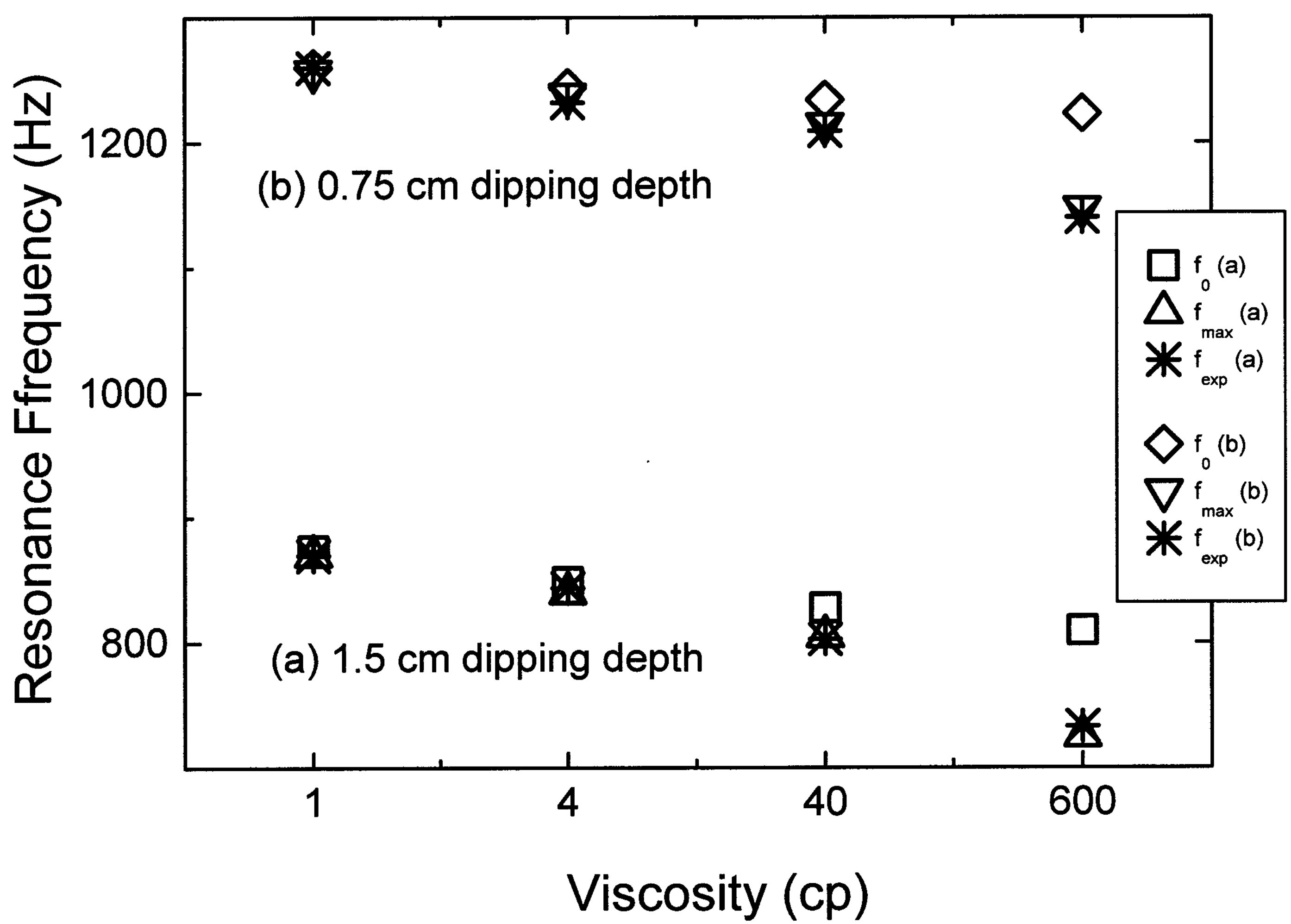


$b_{in}/2\pi \cong 9.0\times10^{-3}$ Hz/kg

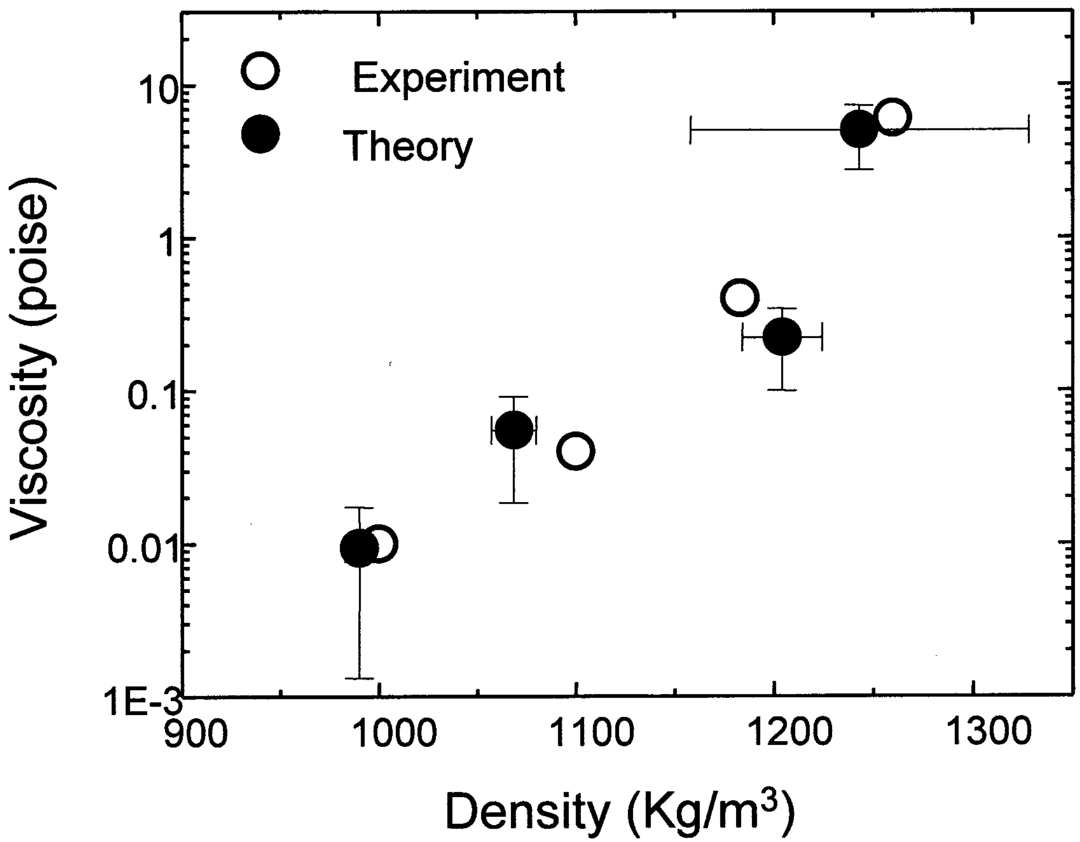
Induced Voltage at Resonance

Input=10V





Resonance Ffrequency (Hz)
1200
1000
800
(b) 0.75 cm dipping depth
(a) 1.5 cm dipping depth
1
4
40
600
Viscosity (cp)
f 0 (a)
f max (a)
f exp (a)
f 0 (b)
f max (b)
f exp (b)


Experiment
Theory
Viscosity (poise)
10
1
0.1
0.01
1E-3
900
1000
1100
1200
1300
Density (Kg/m3)

Size effect: Scaling Analysis

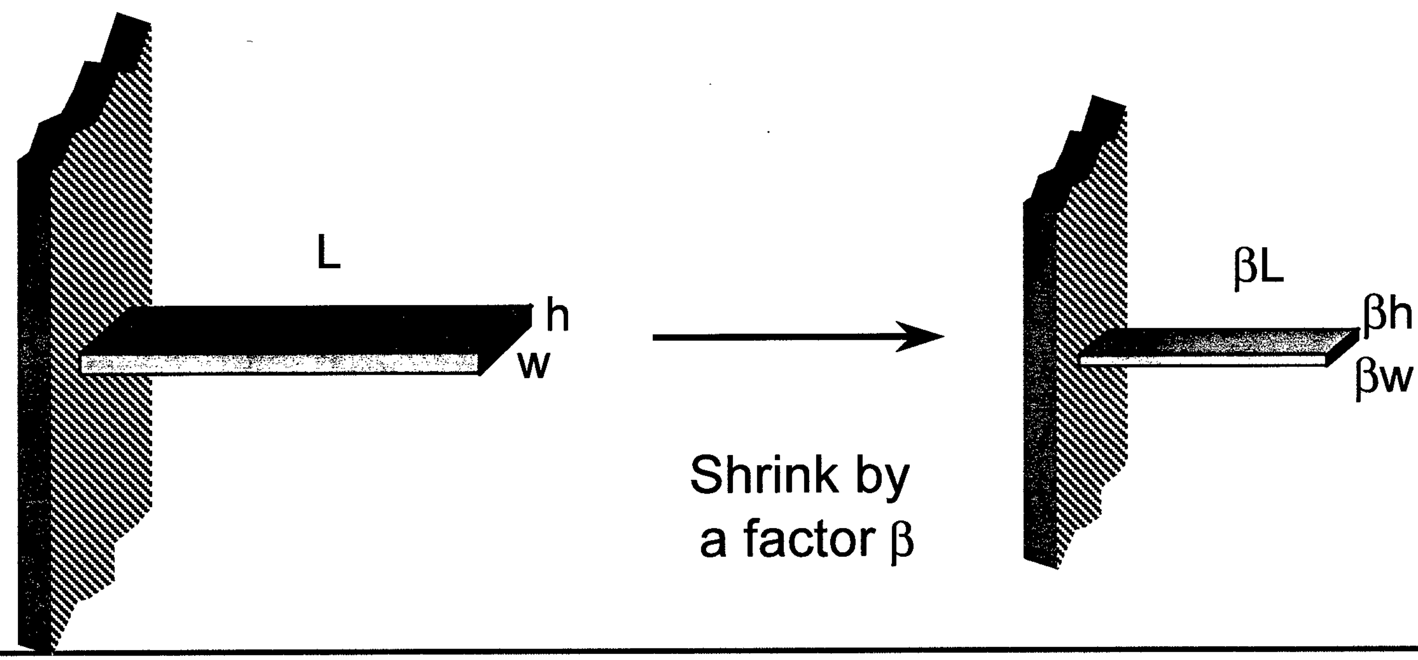
With 1.5 cm dipping depth

$MI = 1.0\times10^{-3}$ in water

$= 1.97\times10^{-3}$ kg, in 75 wt % glycerol

$Me = 3.09\times10^{-4}$ kg

Only MI is considered



$$K(\beta) \propto \beta K$$

(1) High-frequency low-viscosity

$$MI_\infty(\beta) \propto \beta^3 MI_\infty$$

$$f_i(\beta) \approx \sqrt{\frac{K(\beta)}{MI_\infty(\beta)}} \propto \beta^{-1} f_i$$

The damping factor

$$b_\infty(\beta) \propto \beta^{3/2} b_\infty$$

$$\gamma_{liq}(\beta) = \beta^{-3/2} \gamma_{liq}$$

$$Q(\beta) = \frac{f_{max}}{\gamma} \propto \beta^{1/2} Q$$

(2) Low-frequency, high-viscosity

$$MI_0(\beta) \propto \beta^2 f_i^{-1/2}$$

$$f_i(\beta) \propto \sqrt{\frac{K(\beta)}{MI_0(\beta)}} \propto \beta^{-1/2} (f_i(\beta))^{1/4}$$

$$\Rightarrow f_i(\beta) \propto \sqrt{\frac{K(\beta)}{MI_0(\beta)}} \propto \beta^{-2/3}$$

$$\Rightarrow MI_0(\beta) \propto \beta^{7/3}$$

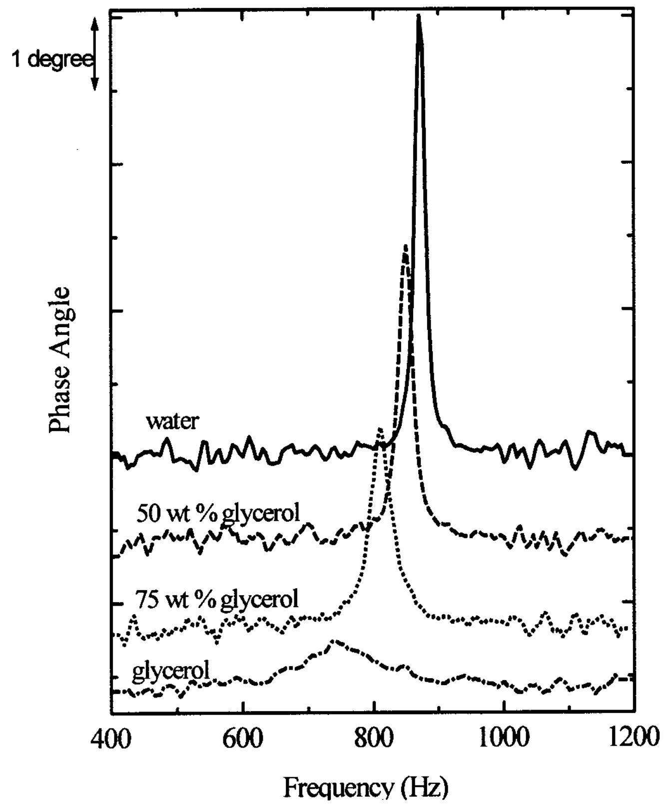
The damping factor

$$b_0(\beta) \propto \beta^1 b_0$$

$$\gamma_{liq}(\beta) = \frac{b_0(\beta)}{MI_0(\beta)} \propto \beta^{-4/3}$$

$$Q(\beta) = \frac{f_{max}}{\gamma} \propto \beta^{2/3}$$

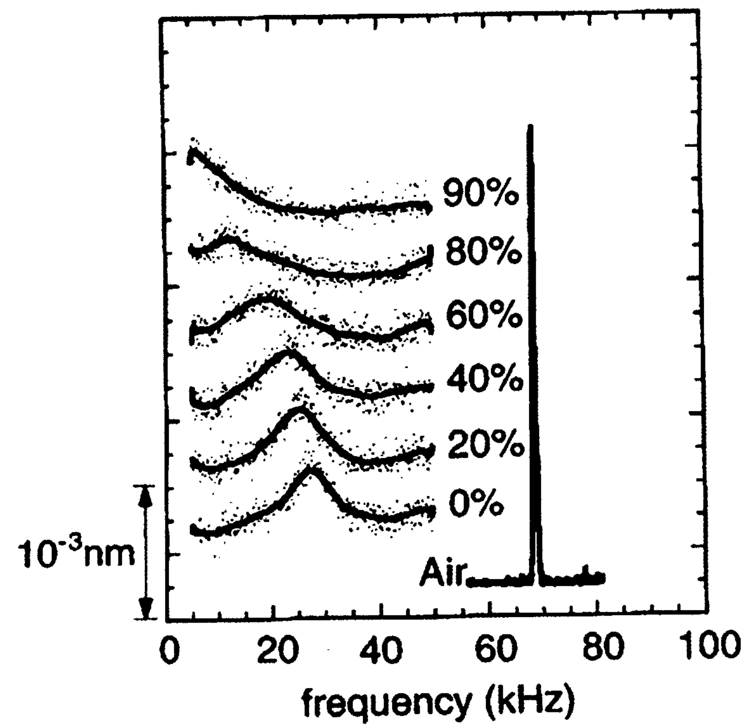
Present cantilever



L=3cm

f_{water}= 870 Hz
$f_{glycerol}$= 700 Hz
$\Delta f/ f_{water}$ = 30%

Microcantilever



P. I. Oden et al., Appl. Phys. Lett. 68(26), 3814-3816 (1996).

L=100μm

f_{water}= 25 kHz
$f_{glycerol}$= 5 kHz
$\Delta f/ f_{water}$ = 80%

Conclusions

(1) *Piezoelectric cantilevers can effectively sense the change in the liquid* viscosity and density.

(2) *The liquid viscosity and density can be accurately determined by the oscillating-sphere model.*

(3) *Miniaturized cantilevers are more sensitive to liquid viscosity and density change (both in terms of resonance-frequency shift and peak broadening).*

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Dynamics of Piezoelectric Cantilevers-Size Effects

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AND ARTHUR BALLATO‡

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FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

Department of Chemical Engineering and
Princeton Materials Institute
Princeton University

Dynamics of Piezoelectric Cantilevers–Size Effects

P. C. Y. Lee,[†] R. Huang,[†] N. Liu,[†] and A. Ballato[‡]

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Princeton Materials Institute
Princeton University, Princeton, NJ 08544-5263

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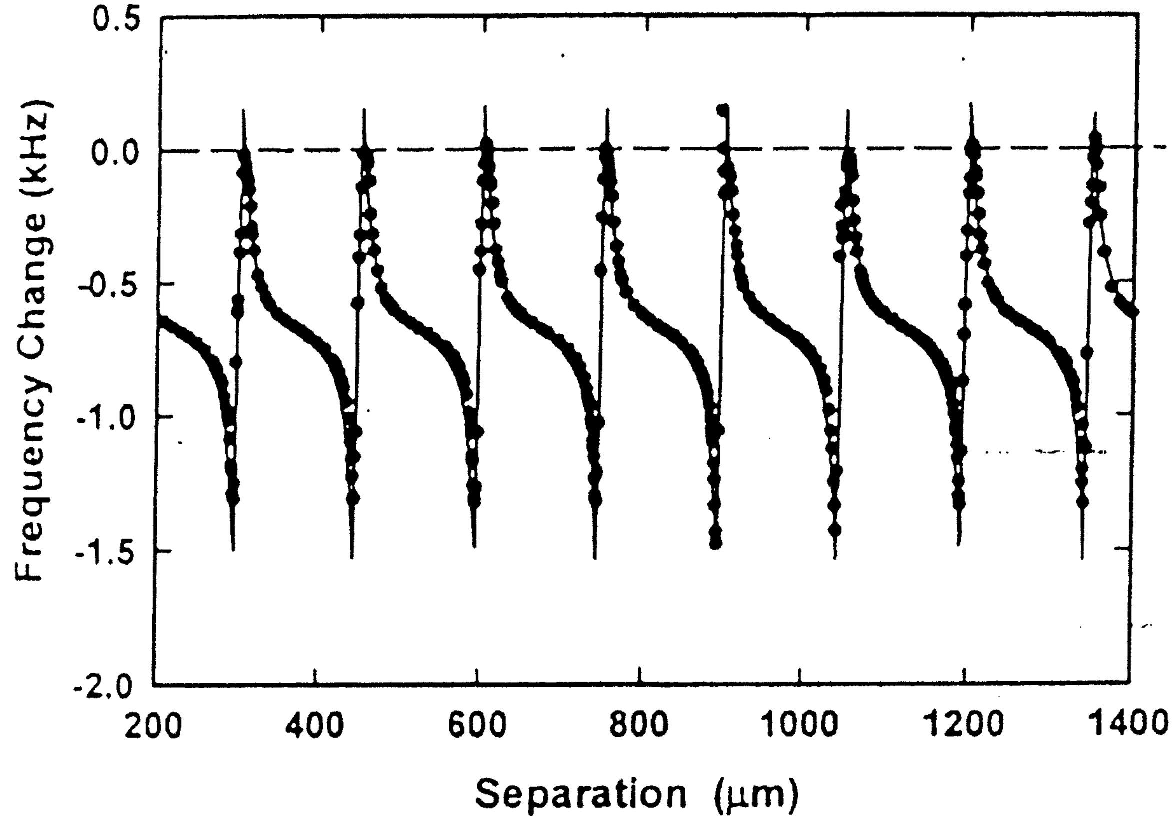
AMSEL-RD-CS, Fort Monmouth, NJ 07703

Dynamics of Piezoelectric Shell Transducers

- ***Objectives***
  - Model and analyze piezoelectric plate and shell resonators with thickness-graded properties
  - Examine and understand sensitivities of resonance frequencies to changes in properties or deposits on faces
- ***Approach***
  - Deduce system of 2-D governing equations
  - Study finite plate problems and compare with data
  - Model and analyze resonators for sensors and actuators
- ***New Achievements***
  - Solution of thickness-shear vibrations for quartz sensors
  - 3-D theory of piezoelectricity with loss mechanisms



- ***Future Studies***
  - **Continue study on the effects of liquid and solid layers on frequencies of resonators for sensing applications**
  - **Study vibrations and attenuations of ceramic resonators by including dissipation (e.g., internal friction and DC conductivity)**
  - **Study vibrational characteristics of micro-PZT beams for actuating and sensing applications**

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Synthesis and Characterization of PMN-PT Piezoelectrics

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Synthesis and Characterization of PMN-PT Piezoelectrics

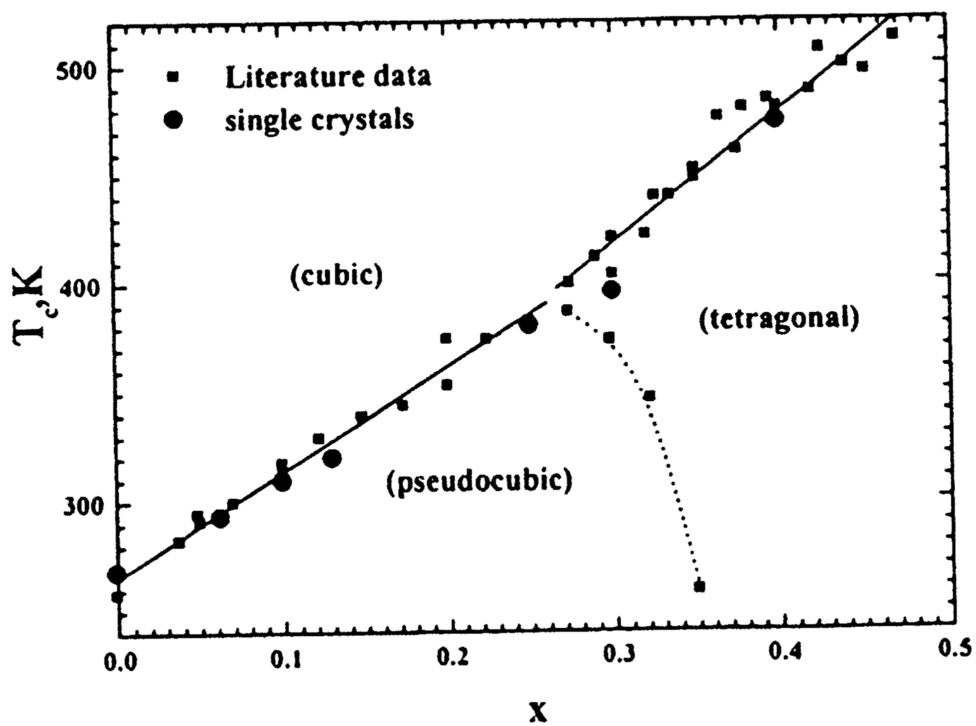
Huiming Gu, Wan Y. Shih, and Wei-Heng Shih

Drexel University

Supported by ARO/MURI, DAAH04-95-1-0102

Prin-Drex actuators: PZT/PZT, PZT/ZnO → High displacement due to domain switching at high electric fields

PMN-PT is potentially more effective than PZT



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PMN-PT: multi-layer capacitors and electrostrictive applications

Difficult to obtain single-phase perovskite: presence of pyrochlore phase

Columbite method: Swartz and Shrout (1982)
Prevention of reactions between Nb_2O_5 and PbO.

$$MgO + Nb_2O_5 \xrightarrow{1000°C} MgNb_2O_6$$

$$MgNb_2O_6 + 3PbO \xrightarrow{700°C} 3Pb(Mg_{1/3}Nb_{2/3})O_3$$

S. L. Swartz and T.R. Shrout, *Mater. Res. Bull.*, Vol 17, 1245-1250, (1982).

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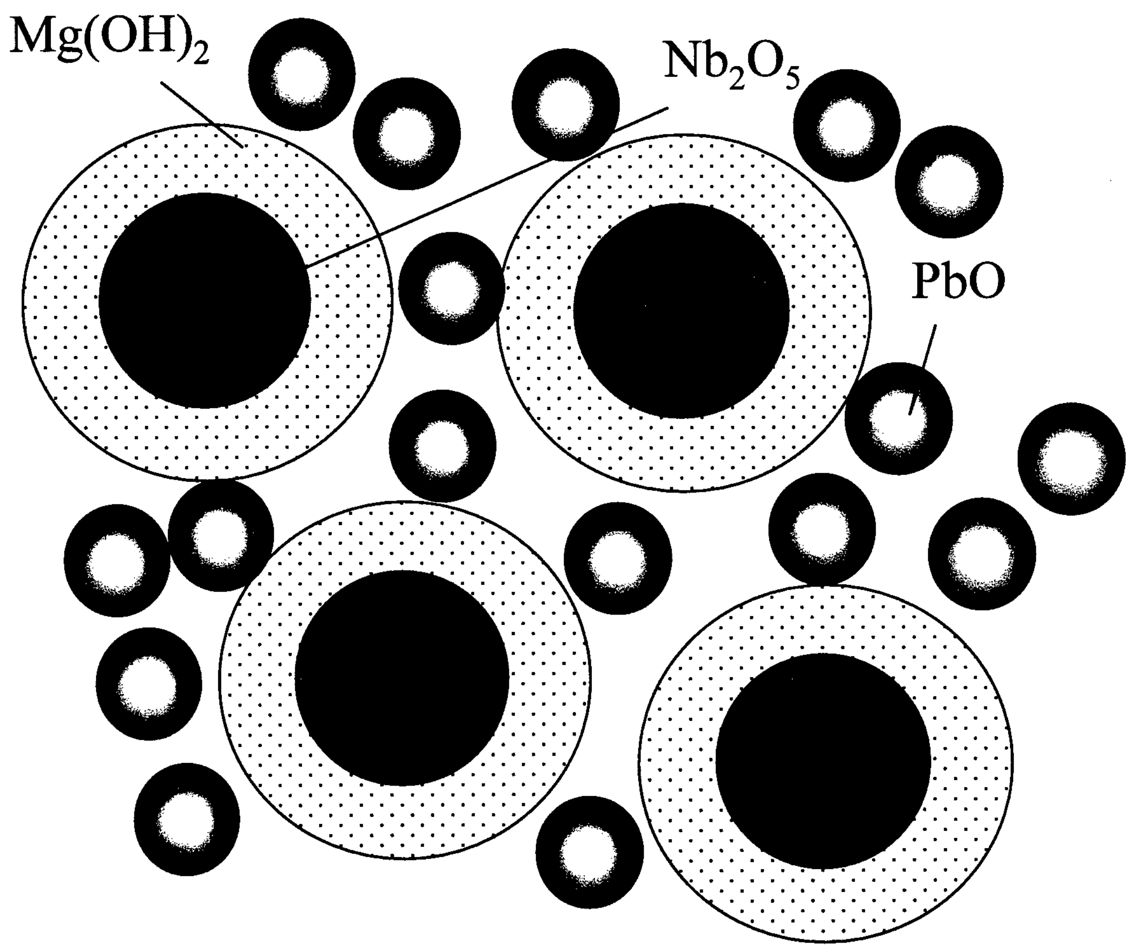
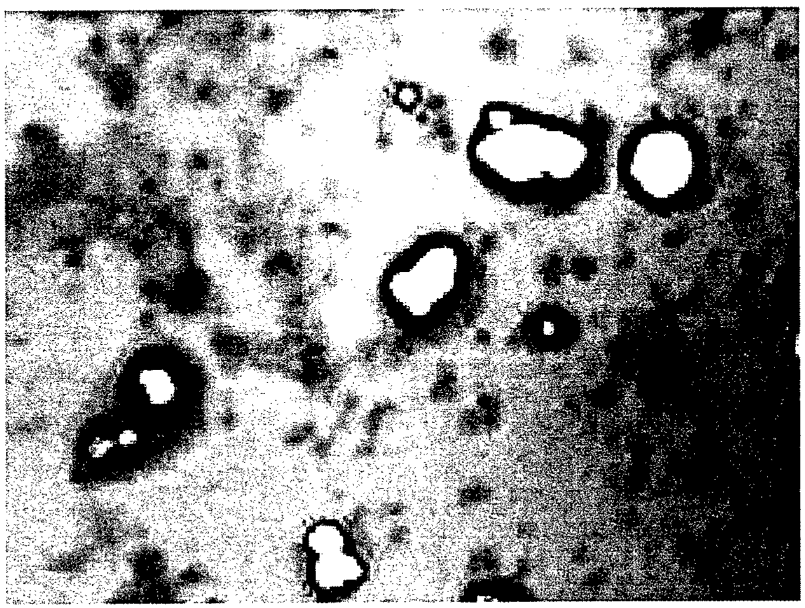
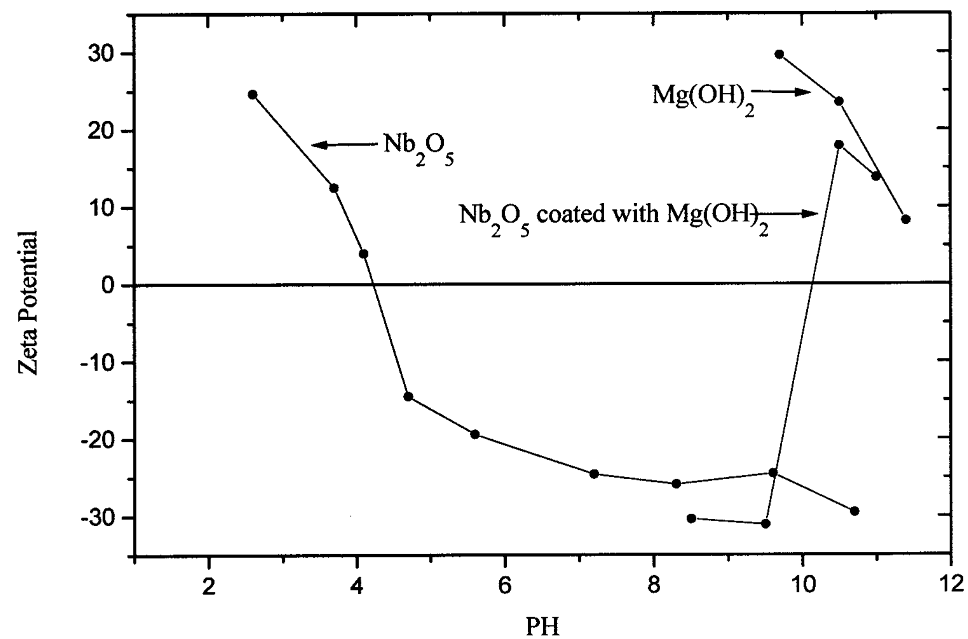
Our approach: Coating of Nb_2O_5 powder with $Mg(OH)_2$, to prevent the interaction between Nb_2O_5 and PbO.

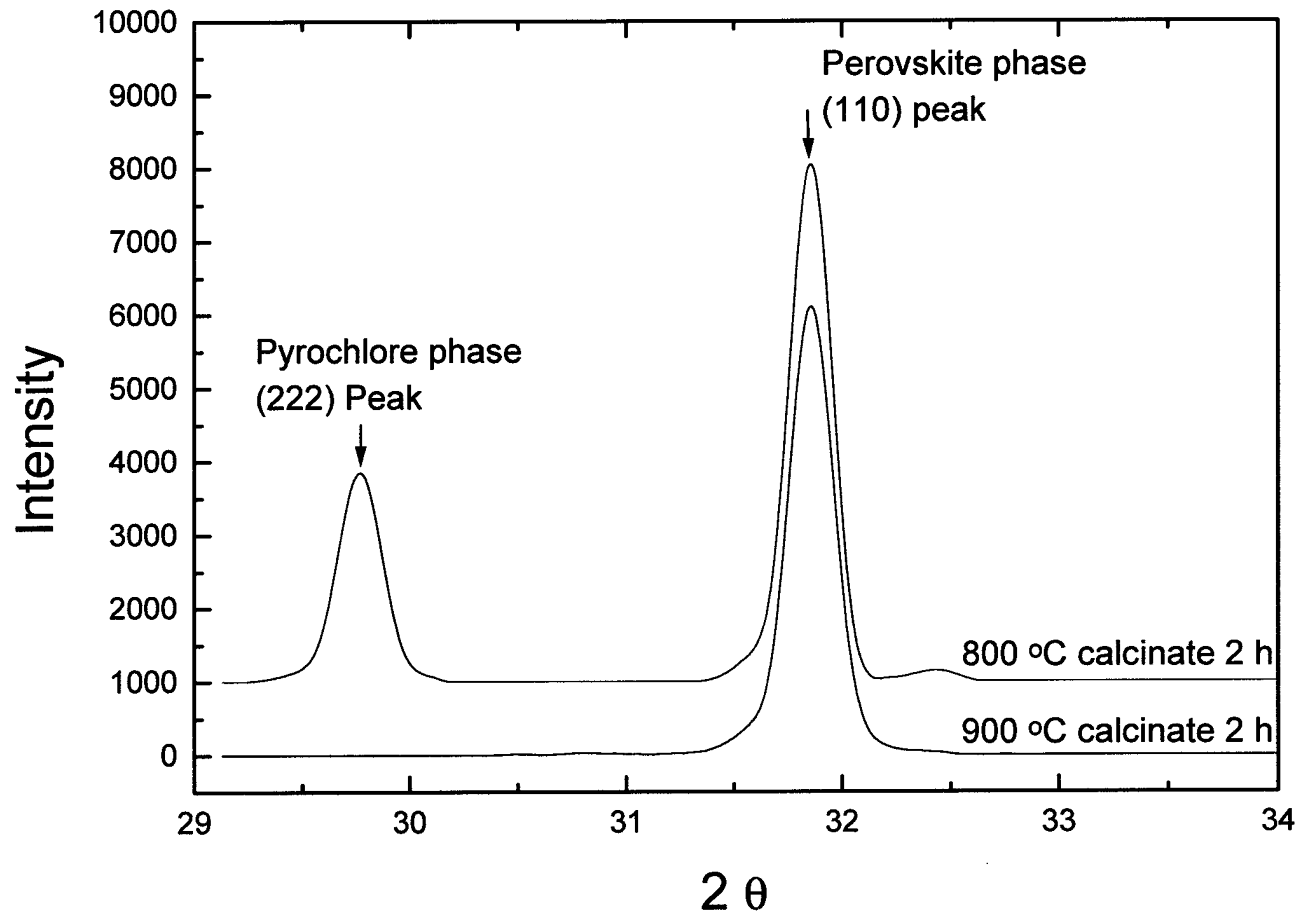


Coating of $Mg(OH)_2$ on Nb_2O_5

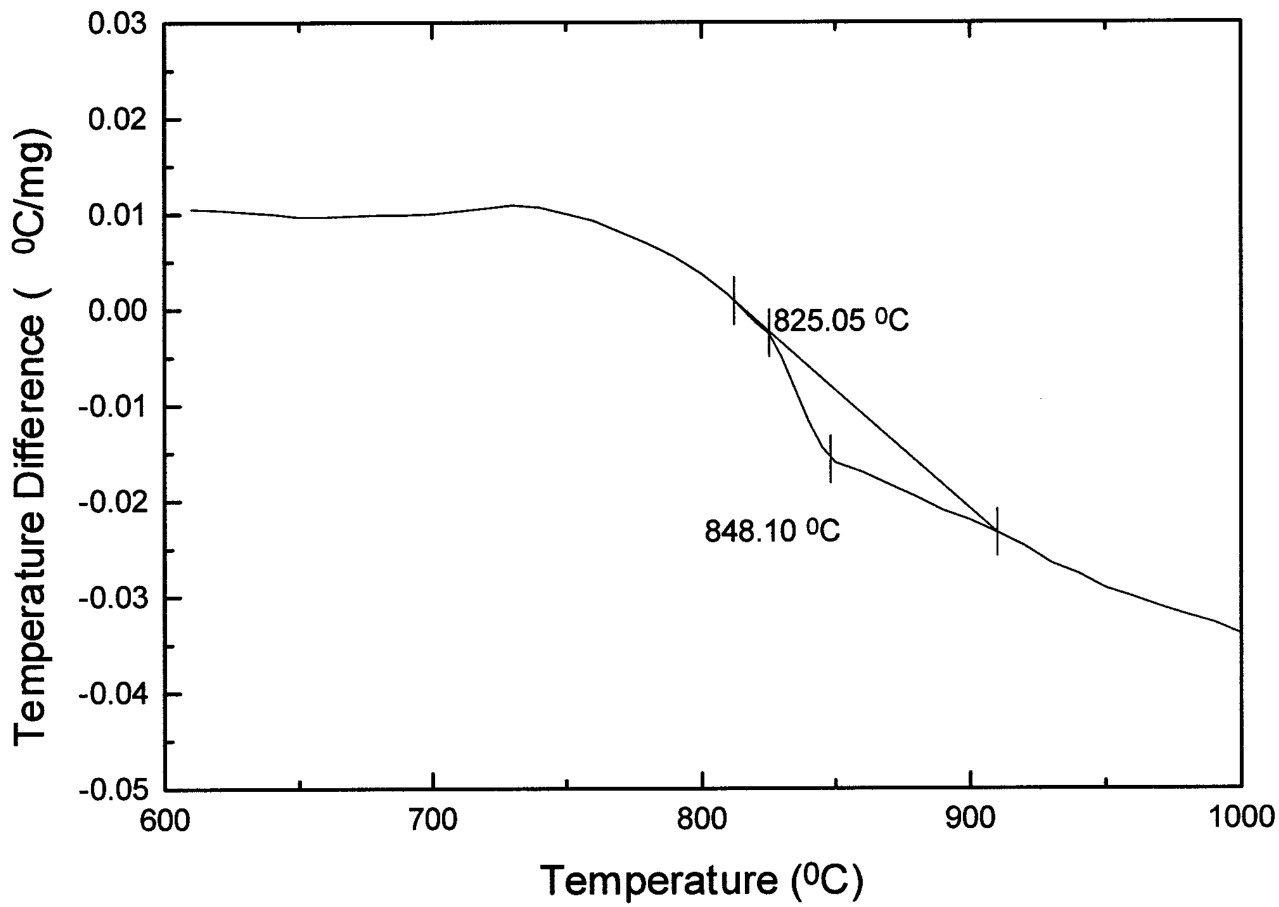




Pyrochlore-free, Perovskite 0.9PMN-0.1PT

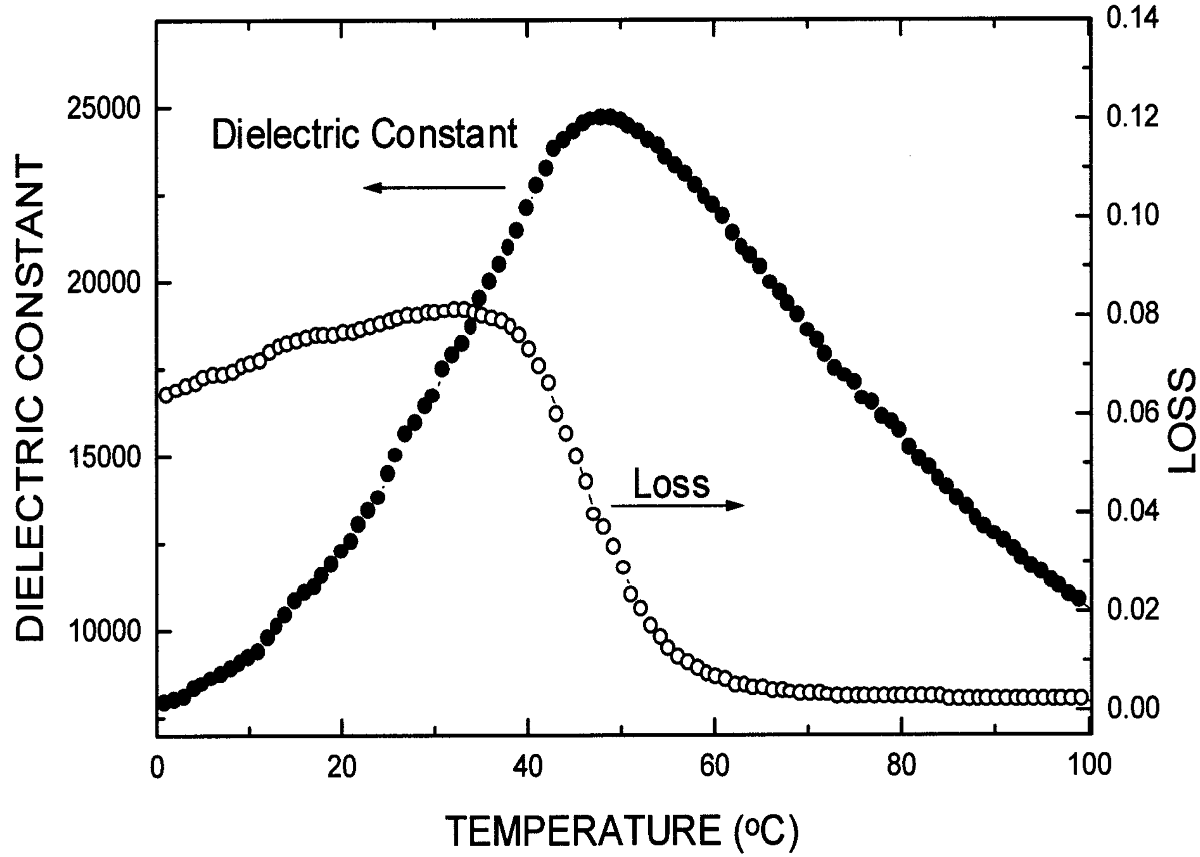


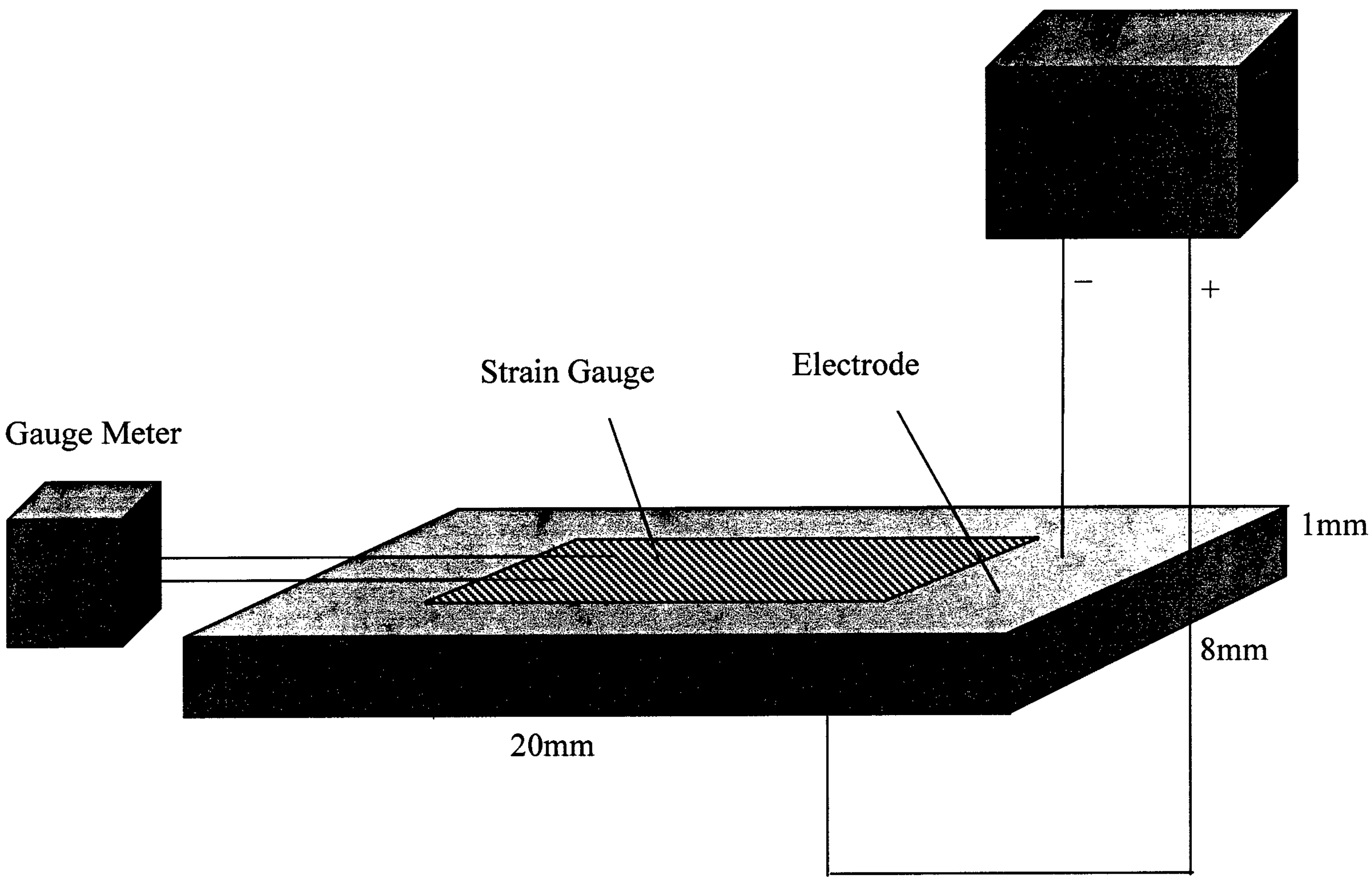
DTA



0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
600
700
800
900
1000
825.05 0C
848.10 0C
Temperature Difference (0C/mg)
Temperature (0C)

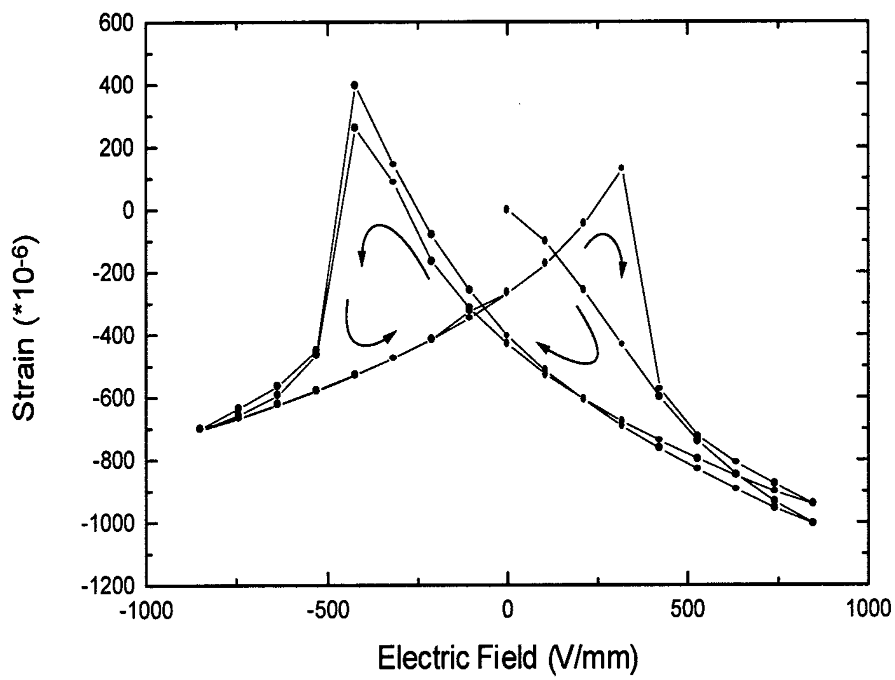
Dielectric constant ~ 24,660 at T_c



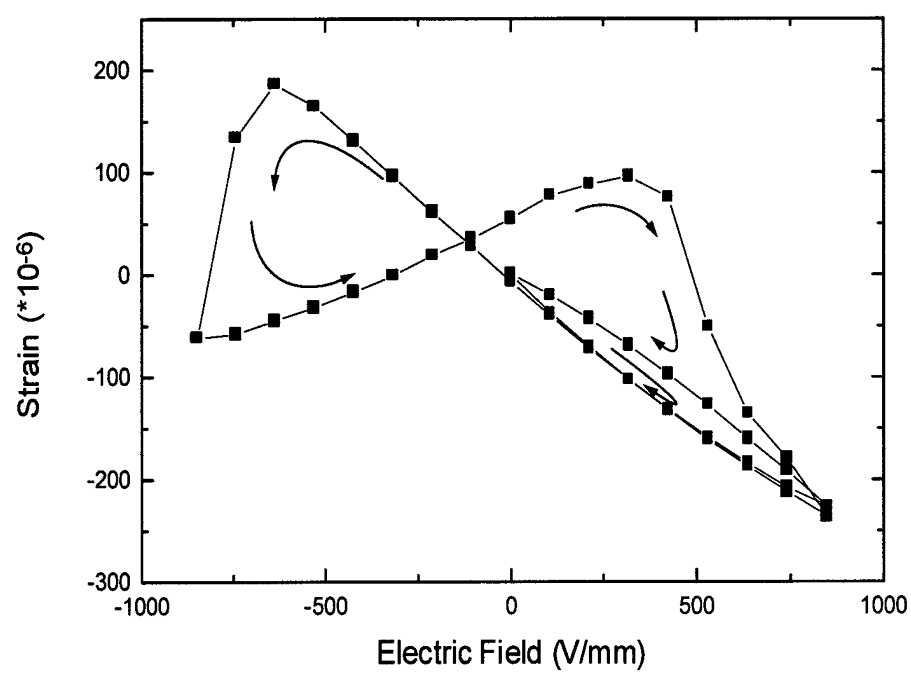

High Voltage Generator
−
+
Strain Gauge
Electrode
Gauge Meter
1mm
8mm
20mm

Strain vs. Electric Field Behavior

EDO powders

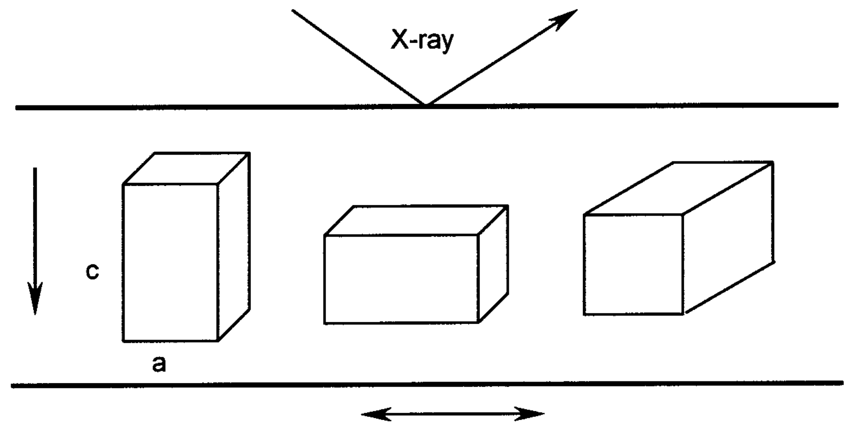


0.6PMN-0.4PT



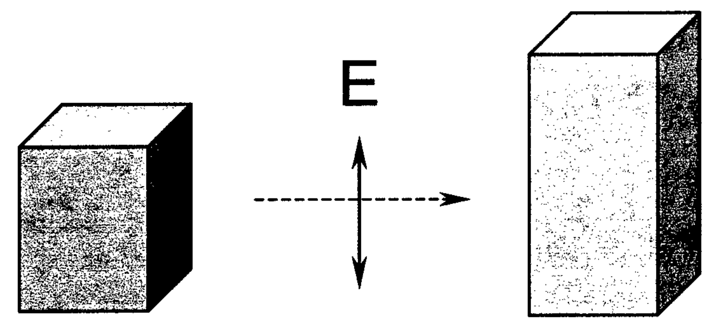
Summary of Properties

	d_{33} (10^{-12} m/v)		d_{31} (10^{-12} m/v) at 800V/mm	Dielectric Constant at room temperature
	At low electric field	At Electric Field of 800 V/mm		
EDO Powder	468.8	7000	1180	4735
0.6PMN-0.4PT	336	Not able to detect	267	3408



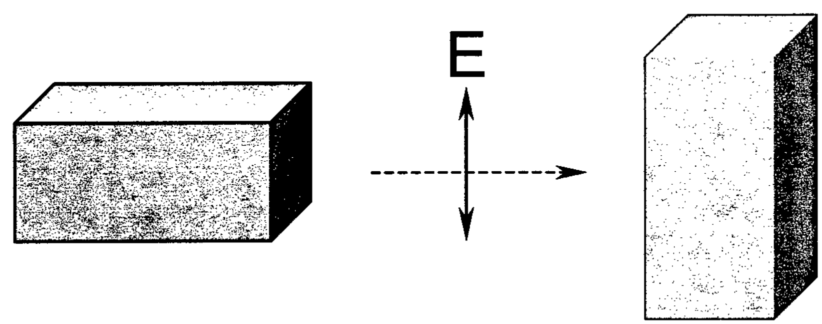
Piezoelectric effect

c and a change with E

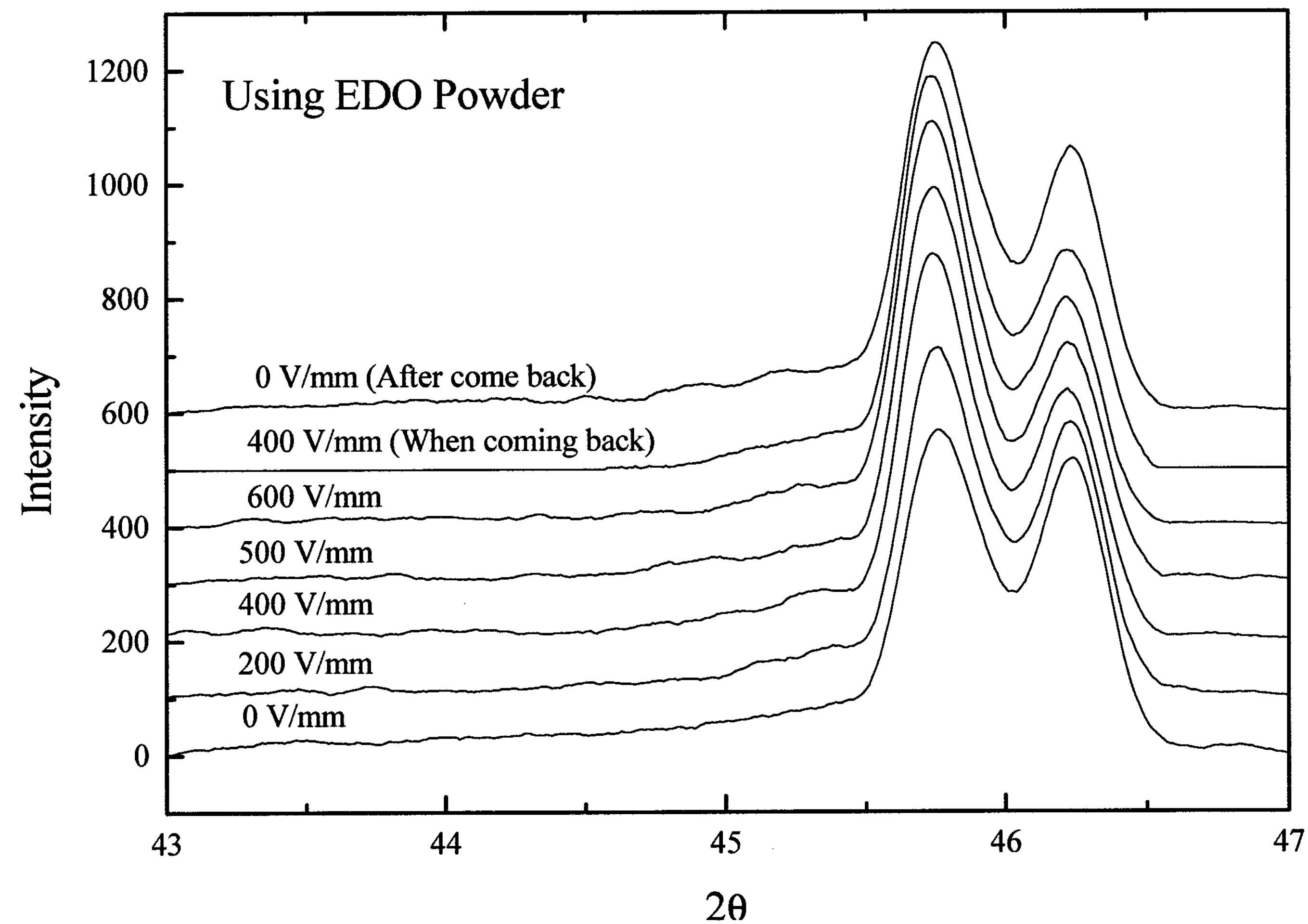


90° Domain switching

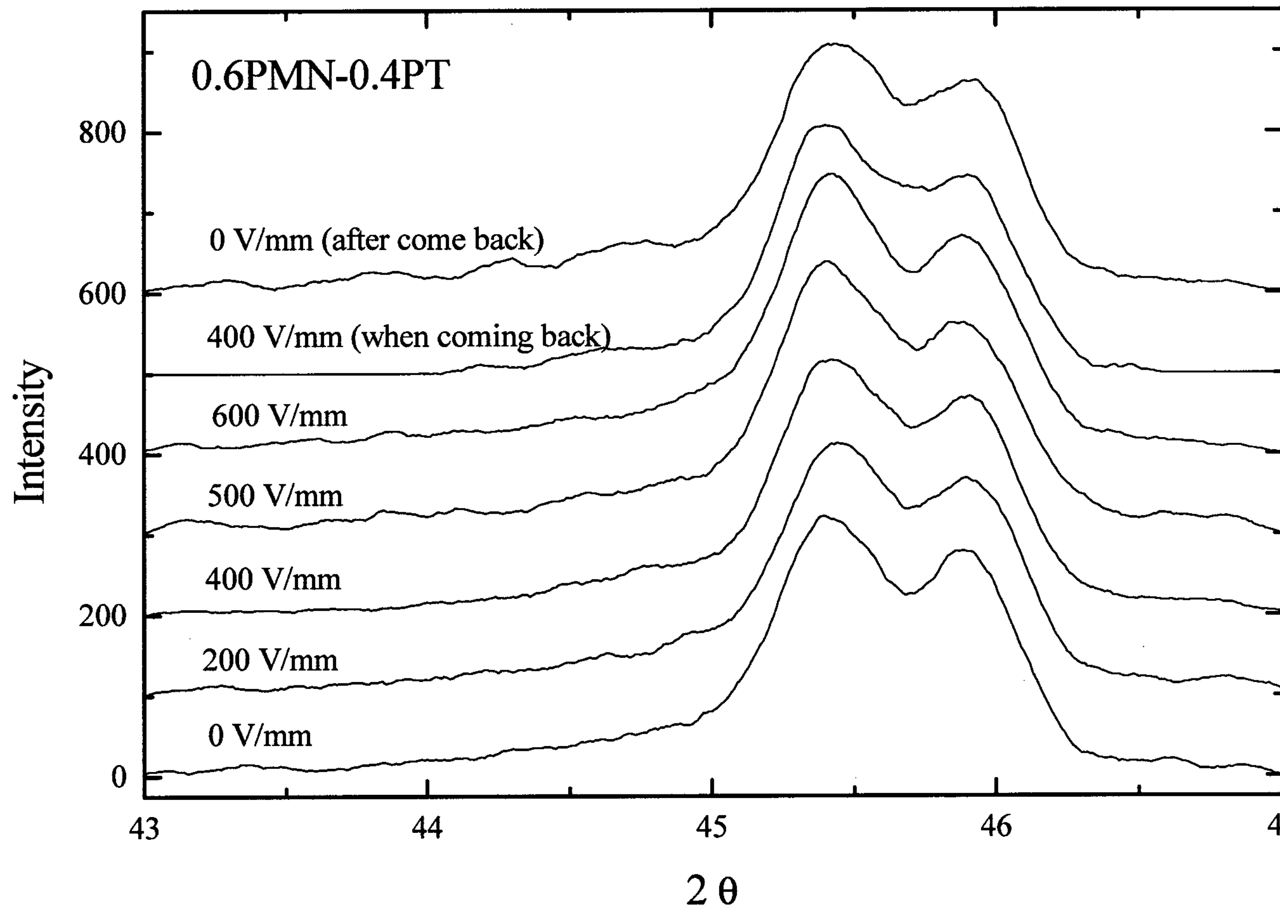
$I_{(002)}/I_{(200)}$ changes with E

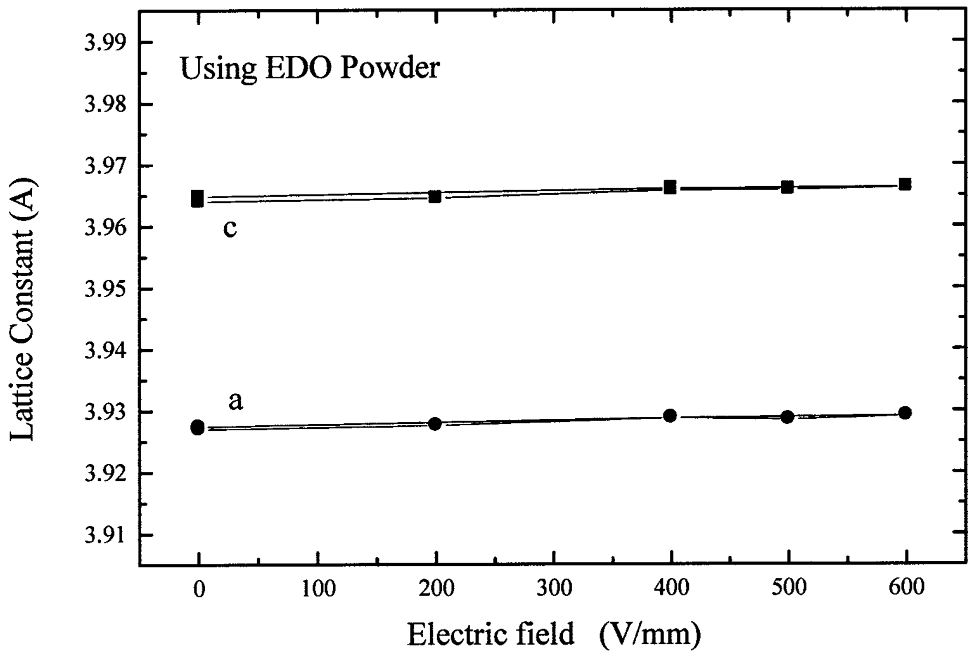


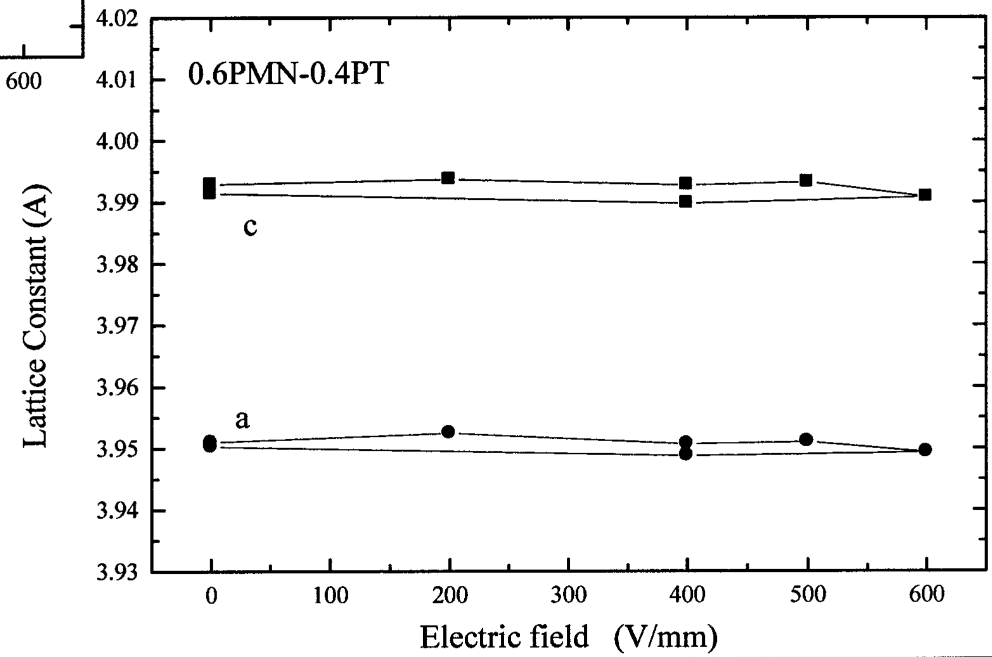
XRD patterns with Electric Fields



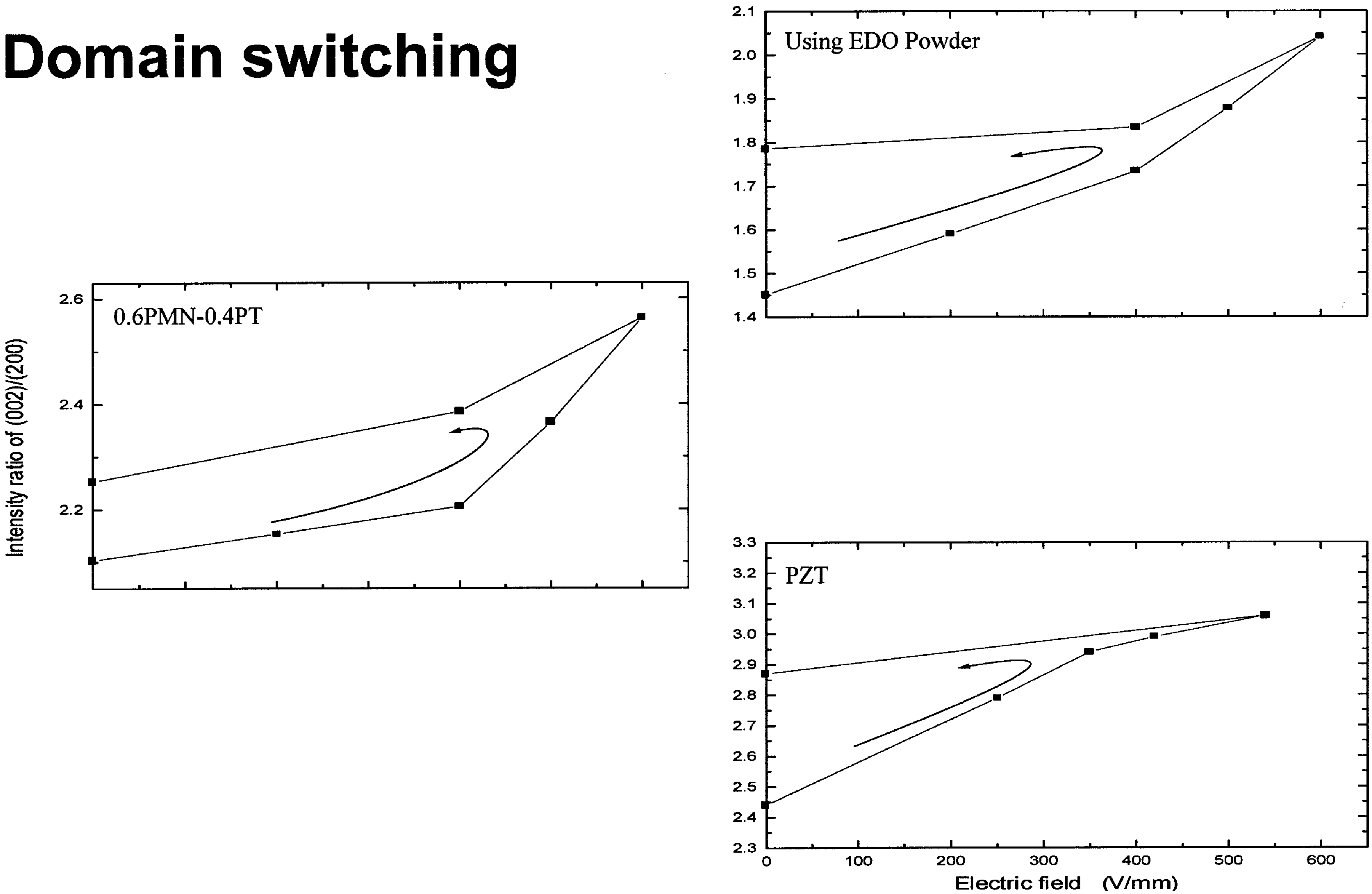
XRD patterns with Electric Fields




Using EDO Powder
c
a
Lattice Constant (A)
3.99
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.91
0
100
200
300
400
500
600
Electric field (V/mm)


0.6PMN-0.4PT
c
a
Lattice Constant (A)
4.02
4.01
4.00
3.99
3.98
3.97
3.96
3.95
3.94
3.93
0
100
200
300
400
500
600
Electric field (V/mm)

Domain switching



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$$R(0)=\frac{I_{0(002)}}{I_{0(200)}}=\frac{C}{A} \qquad R(E)=\frac{I_{(002)}}{I_{(200)}}=\frac{nA+C}{(1-n)A}$$

$$n=\frac{R(E)-R(0)}{1+R(E)}$$

n = fraction of a-domains switched to c-domains

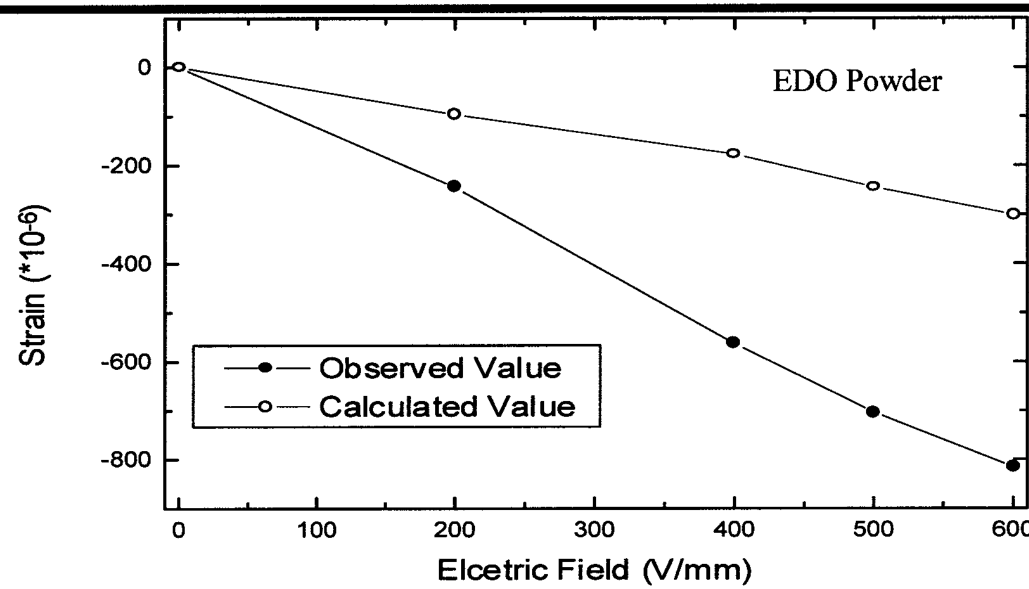
$$S_{1,domain}(E)=\frac{L(E)-L(0)}{L(0)}$$

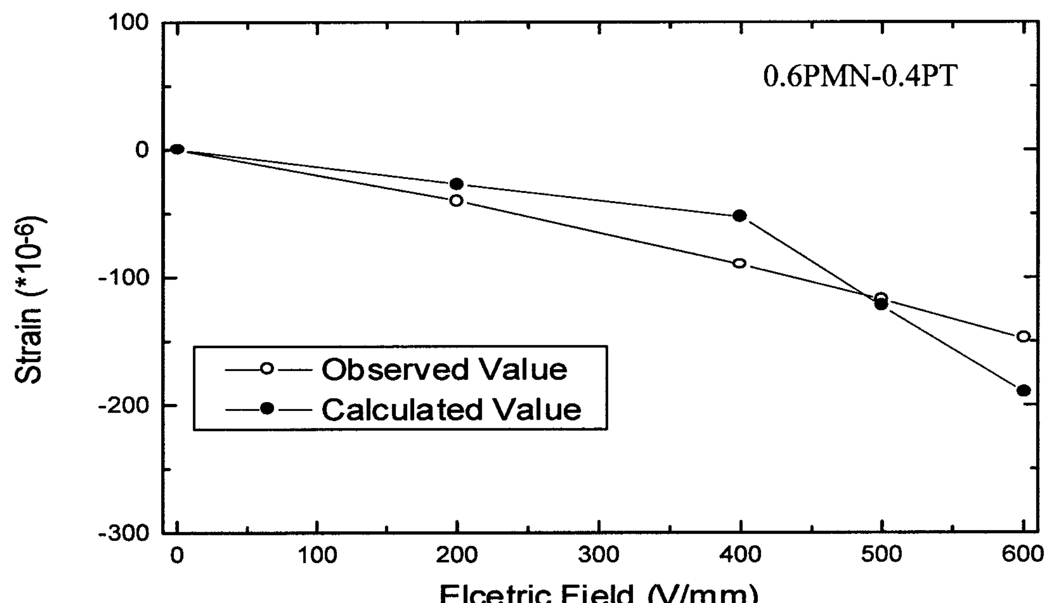
$$L(0)=\eta(0)Ac+(1-\eta(0))Aa+Ca$$

$$L(E)=\eta(E)(1-n)Ac+(1-\eta(E))(1-n)Aa+(C+nA)a$$

Assuming $\eta(0) = \eta(E) = 1/2$,

$$S_1(E)=\frac{(c-a)[R(0)-R(E)]}{[1+R(E)][c+a+2aR(0)]}$$


0
-200
-400
-600
-800
Strain (*10-6)
0
100
200
300
400
500
600
Elcetric Field (V/mm)
EDO Powder
Observed Value
Calculated Value


100
0
-100
-200
-300
Strain (*10-6)
0
100
200
300
400
500
600
Elcetric Field (V/mm)
0.6PMN-0.4PT
Observed Value
Calculated Value

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Conclusions

- *A one-step heating process using $Mg(OH)_2$-coated Nb_2O_5 powders and PbO was developed for synthesizing perovskite PMN-PT*
- *0.6PMN-0.4PT shows significant domain switching behavior at high electric fields*
- *EDO powders show very high d_{33} and d_{31} values at 800 V/mm indicating PMN-PT has great potential for actuator and sensor applications*

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Stereolithography of Organic/ Inorganic Composites

ROBERT K.PRUD'HOMME[*,§], ILHAN A. AKSAY[*,§], DAVID L. MILIUS[*,§], JAMES S. VARTULI[*,§], RAJEEV GARG[*,§] AARON J. DULGAR[*,§], PETER J. PHOTOS[*,§], JAMES LEE[*,§], JAMES LIANG[*,§]

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FIFTH ARO/MURI PROGRAM REVIEW

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CAMBRIDG, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

Rapid Prototyping of Polymer/Ceramic Composites

Robert K. Prud'homme, Ilhan A. Aksay,

Rajeev Garg, Jim H. Lee, Jim Liang,
David L. Milius, Aaron J. Dulgar, and Peter J. Photos

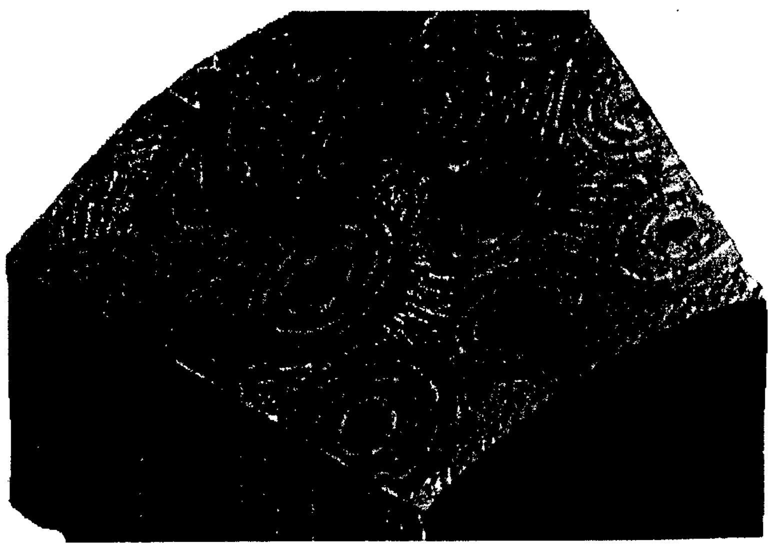
Department of Chemical Engineering and
Princeton Materials Institute,
Princeton University, Princeton, NJ 08544

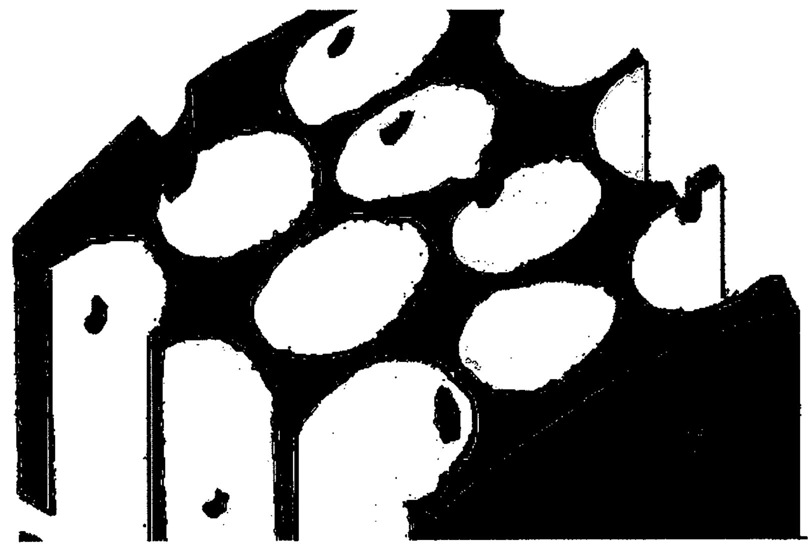
Introduction

[redacted]

- *Goal: Fabrication of ceramic/polymer composites*
- *Case study: bone implants*
  - Stereolithography
  - Biocompatible and mechanically compatible
- *Problems with present bone graft materials:*
  - Autogenous: limited supply, morbidity
  - Allograft: immunogenicity, viral transmission
  - Commercial products: lack bone inductivity and/or strength

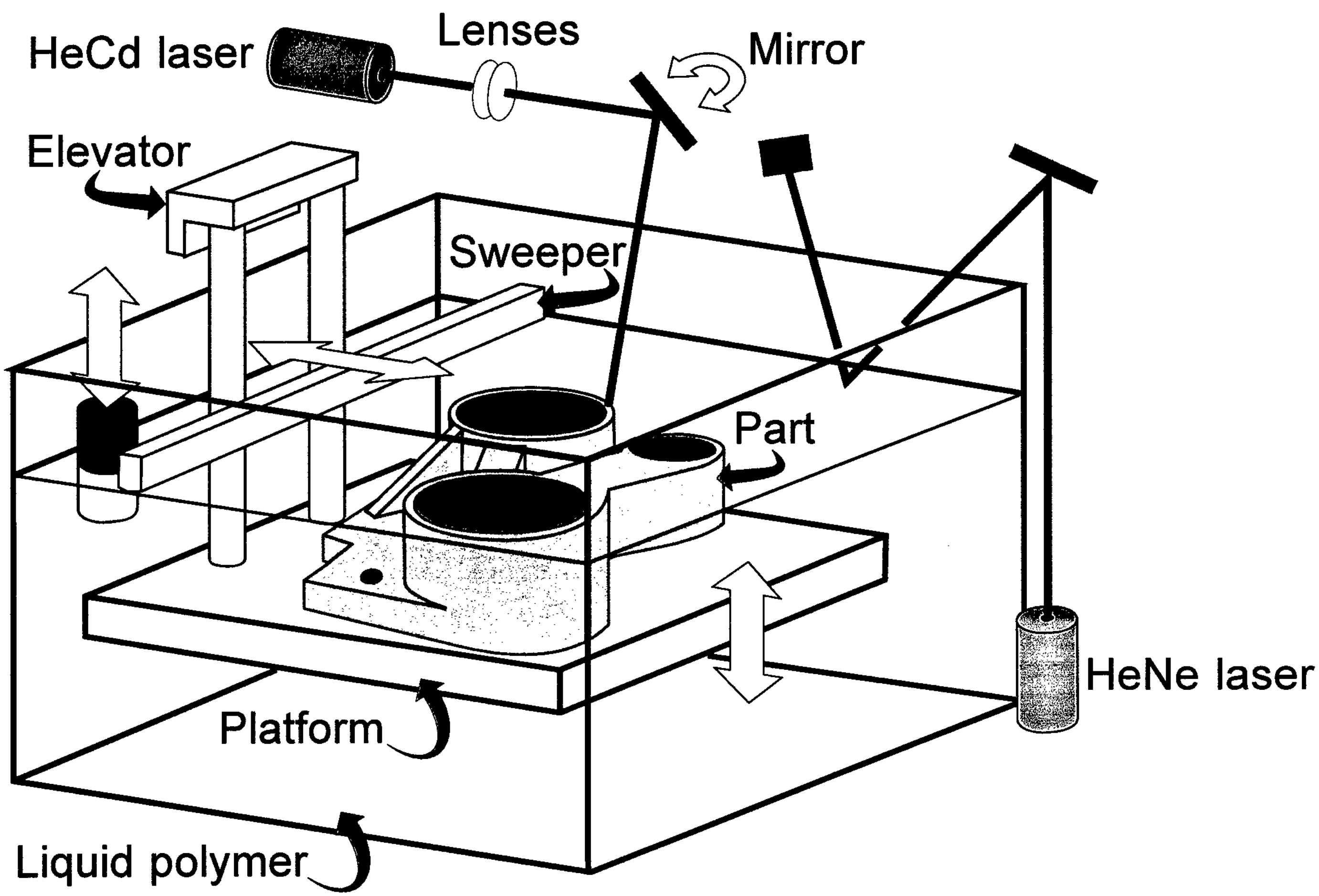
Microstructure of Cortical Bone



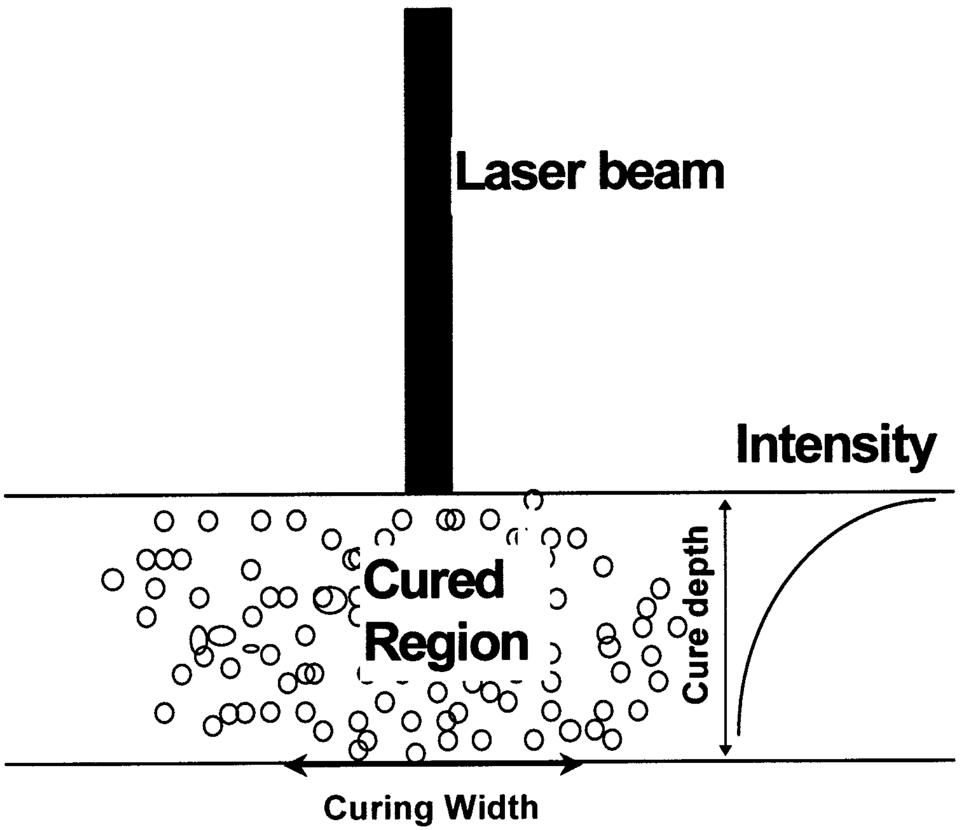


L. L. Hench and J. Wilson, *An Introduction to Bioceramics*
(World Scientific Press, NY 1993)

Stereolithography

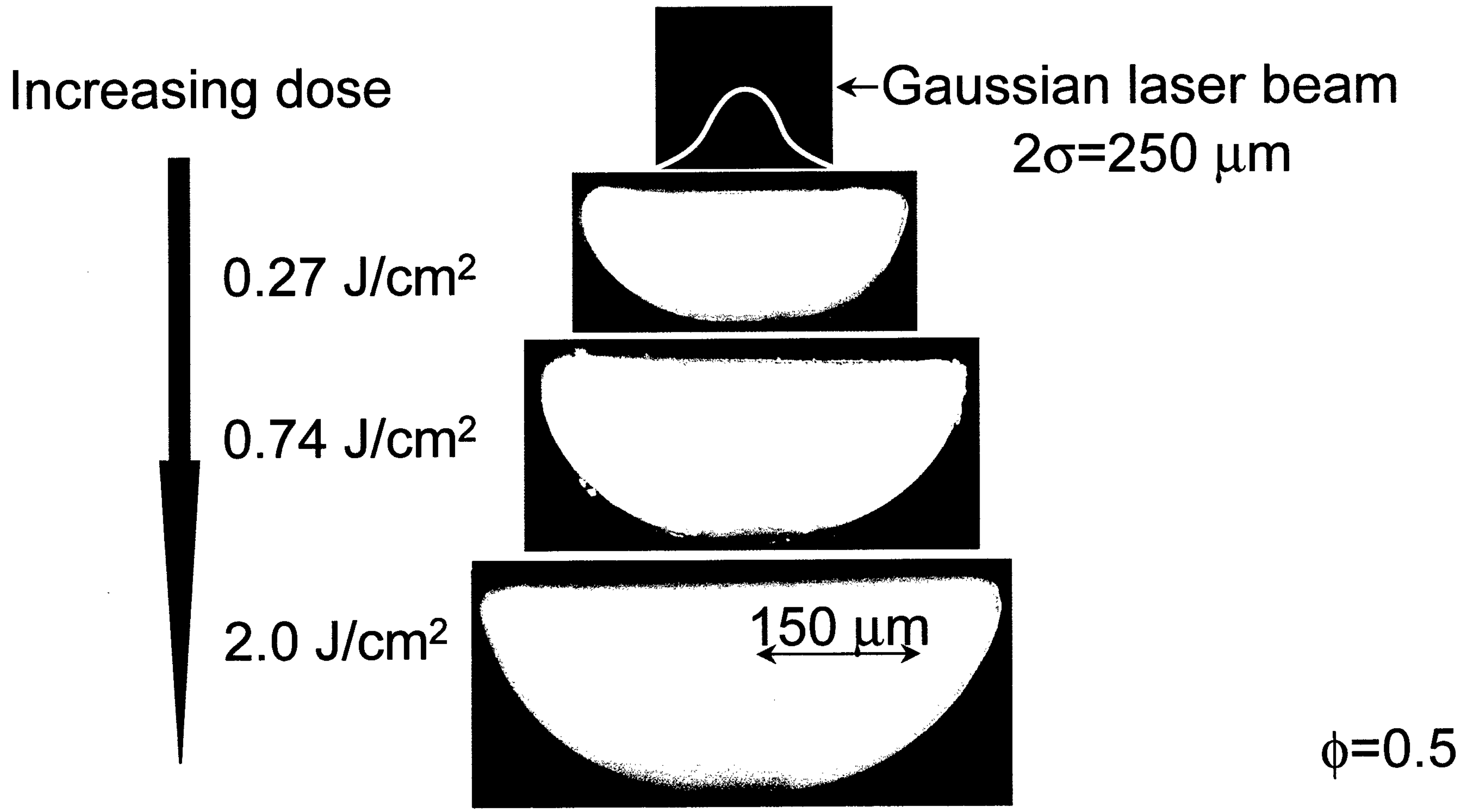


Objective

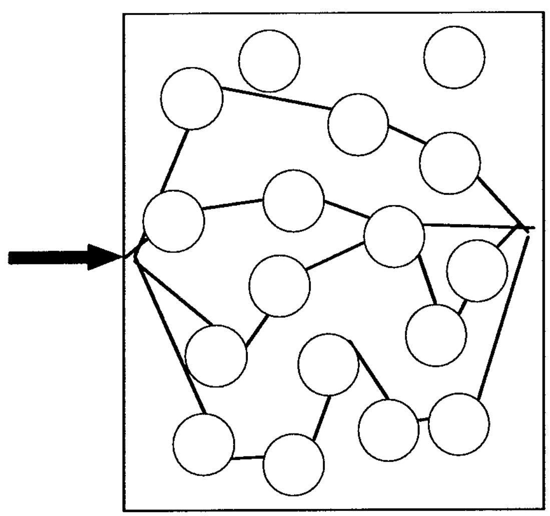


- ***To be able to define the cured profile in a single layer***
- ***Factors controlling curing profile:***
  - **Absorption by photopolymers**
  - **Light scattering from particles**
- ***Requires a model for light propagation in concentrated dispersion***

Curing Profile



Diffusion Model for Scattering



Photons, after going through large number of scattering events, are described as random walkers in the medium.

- ***Photon Density***

$$\frac{\partial I_d}{\partial t} + D\nabla^2 I_d = f(x,y,z,t)$$

$$D = {cl_{tr}}/{3}$$

- ***Transport length***

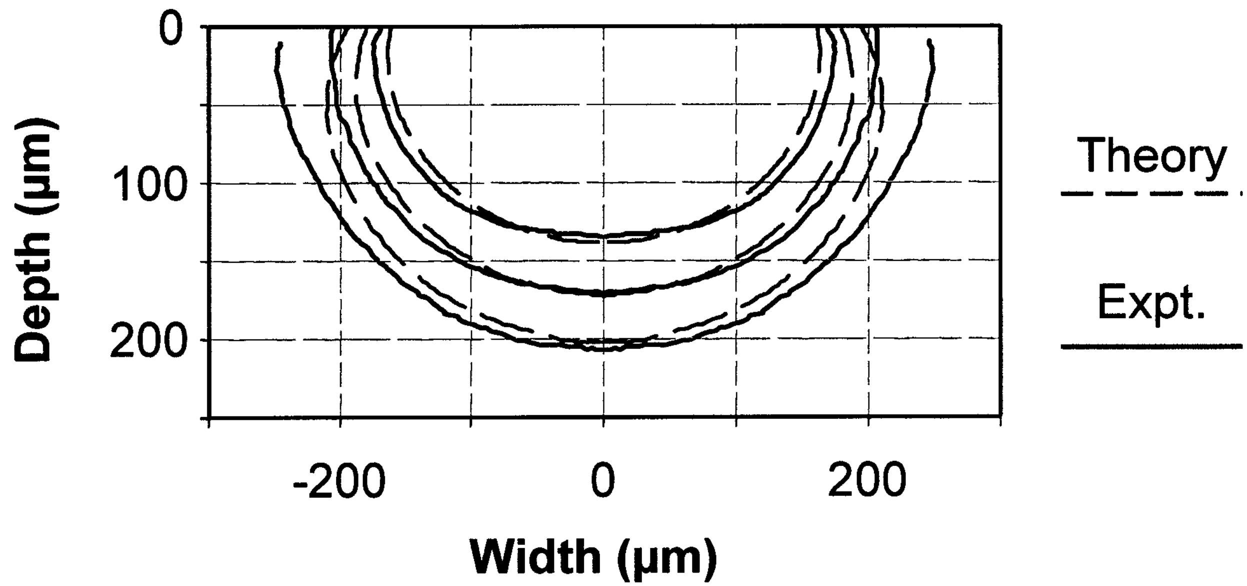
$$l_{tr} = \left(n\sigma_{tr}\left(1-\cos(\theta)\right)\right)^{-1}$$

- ***Correlation from PY***

$$\sigma^* = \int \frac{d\sigma}{d\Omega}\left(1-\cos(\theta)\right) S(\theta)\, d\Omega$$

$$S(\theta) = 1 + n\int \left(g(r)-1\right) e^{iq.r} d^3 r$$

Theory vs Experiment

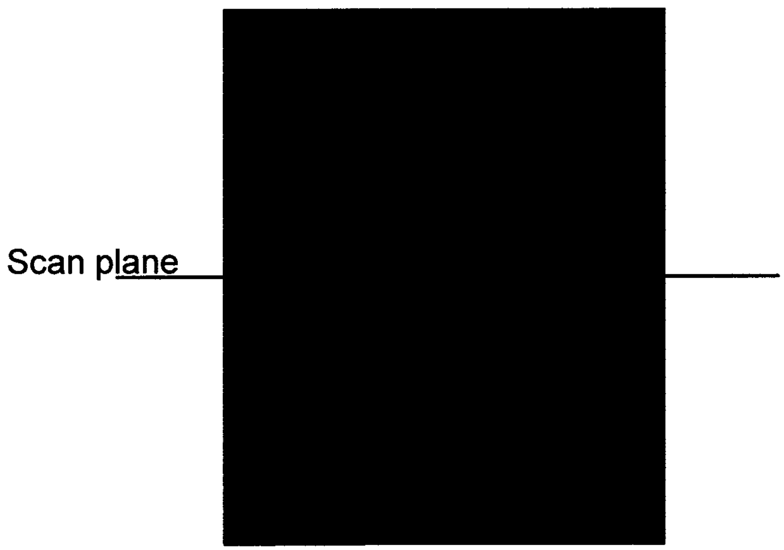


Diffusion theory successfully predicts the curing profile in ceramic dispersion. The experimental profiles are compared with the profiles calculated from diffusion theory:

$$I = \frac{I_0 w^2}{4} \int_0^\infty \exp\left(-\frac{w\lambda}{2\sqrt{2}}\right)^2 J_0(\lambda r) \exp(-(\lambda^2 + D_p^{-2})^{1/2} z) \lambda d\lambda$$

Fabricated Parts

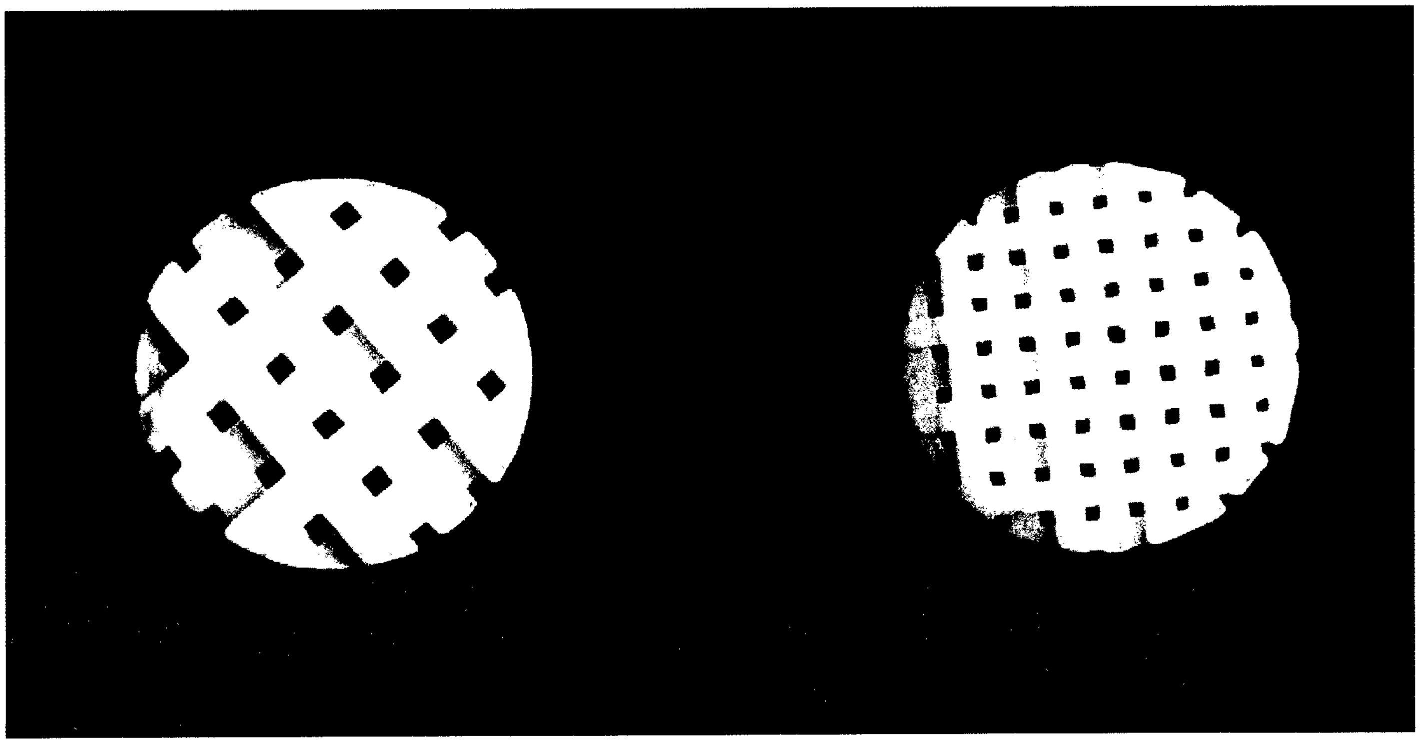
CAT Scan/CAD File



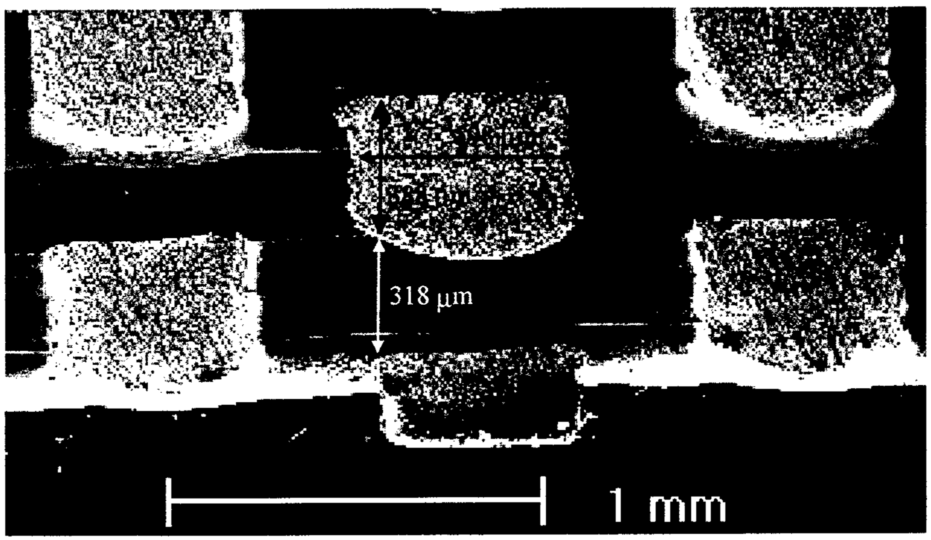
Replicated Part

NIH VH data converted to STL file using "Materialize" software by Ben Dunn at Stratasy's Inc.

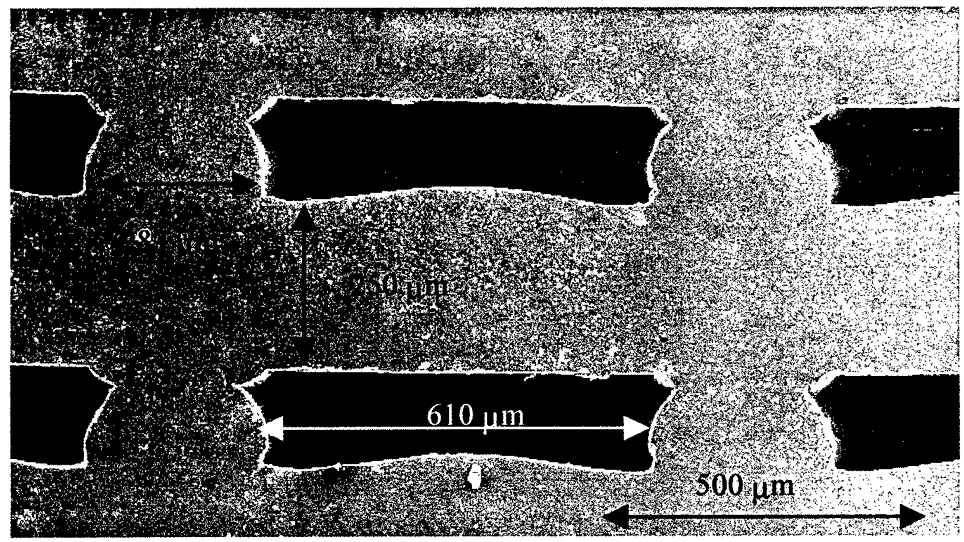
Bone Implant Microstructure



Microstructure of Alumina Implants

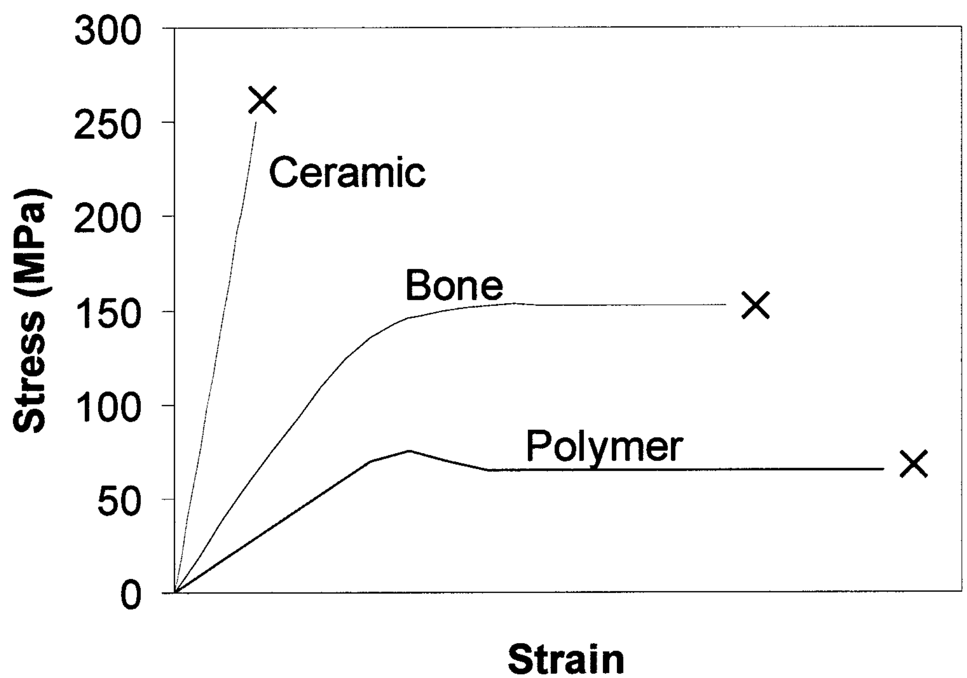


300 μm pore size



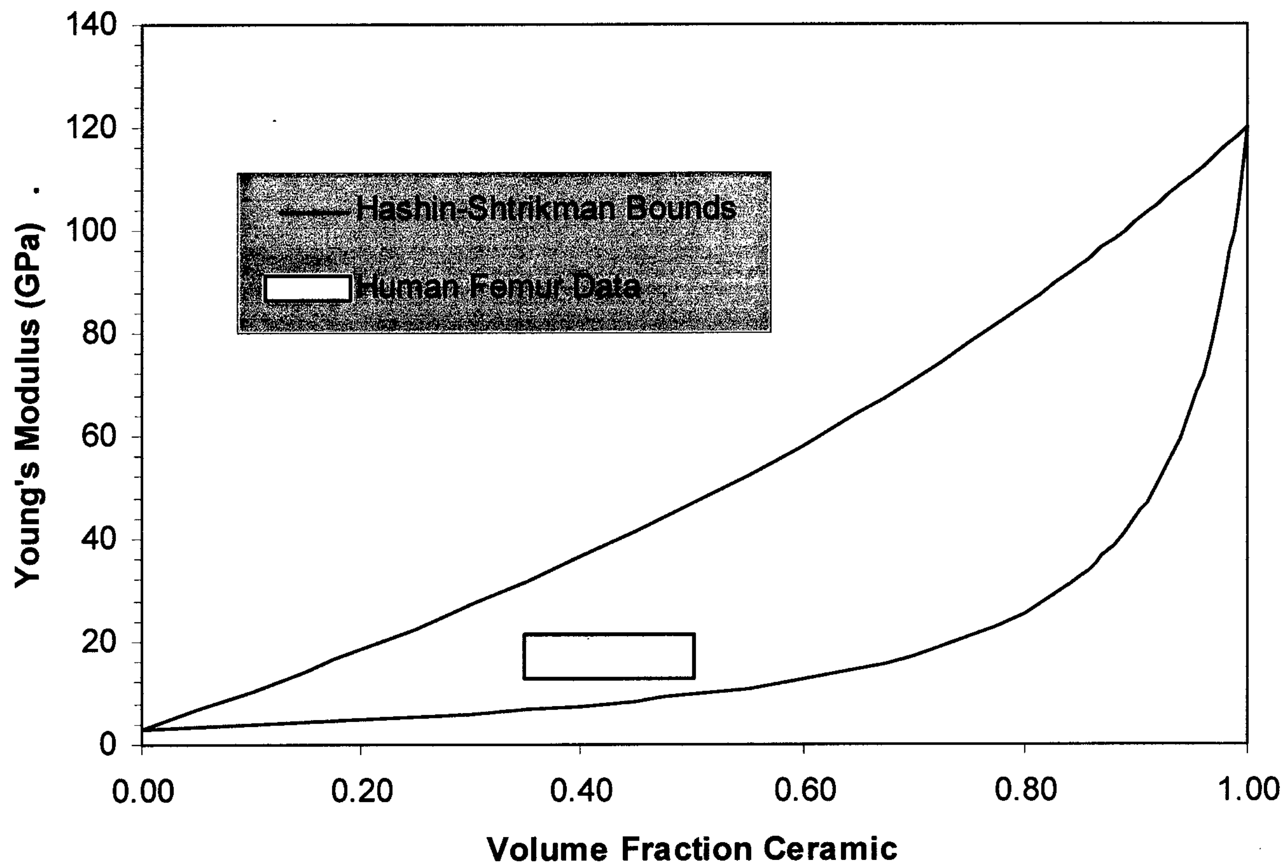
150 μm pore size

Ceramic/Polymer Biocomposites



- ***toughness intermediate between ceramic and polymer***
- ***composite -- 40% hydroxyapatite, 40% collagen, 20% water***

Ceramic/Polymer Biocomposites

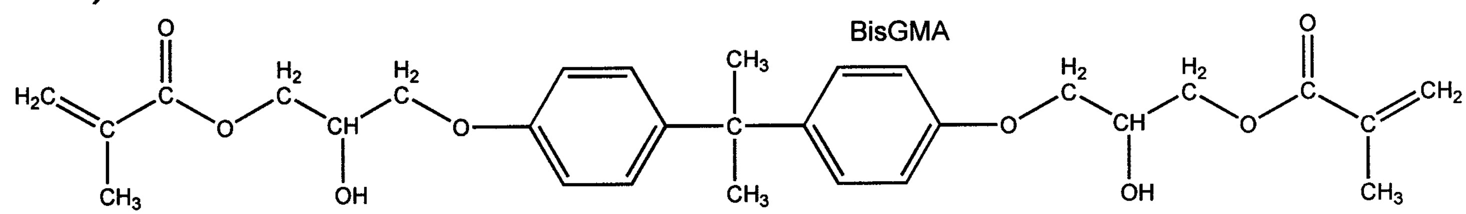


Data: E_P=3 GPa,E_{HA}=120 GPa; Currey. *Mechanical Adaptations of Bones.*

Photochemistry

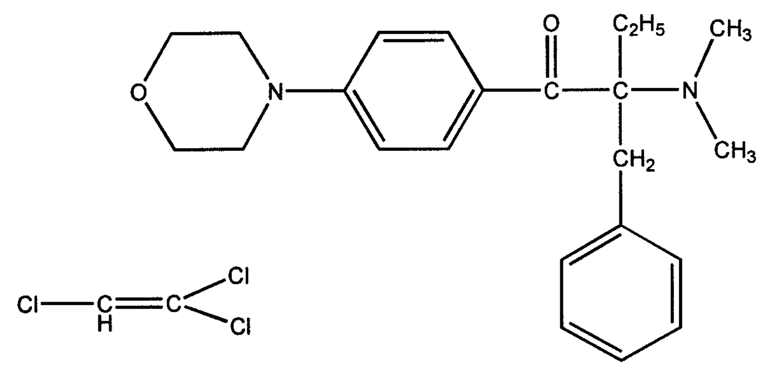
- ***Monomer***
  - *2,2-bis(4-(2-hydroxy-3-methacryloxypropoxy)phenyl) propane (Bis-GMA)*

BisGMA



- ***Photoinitiator***
  - *2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone (DBMP)*

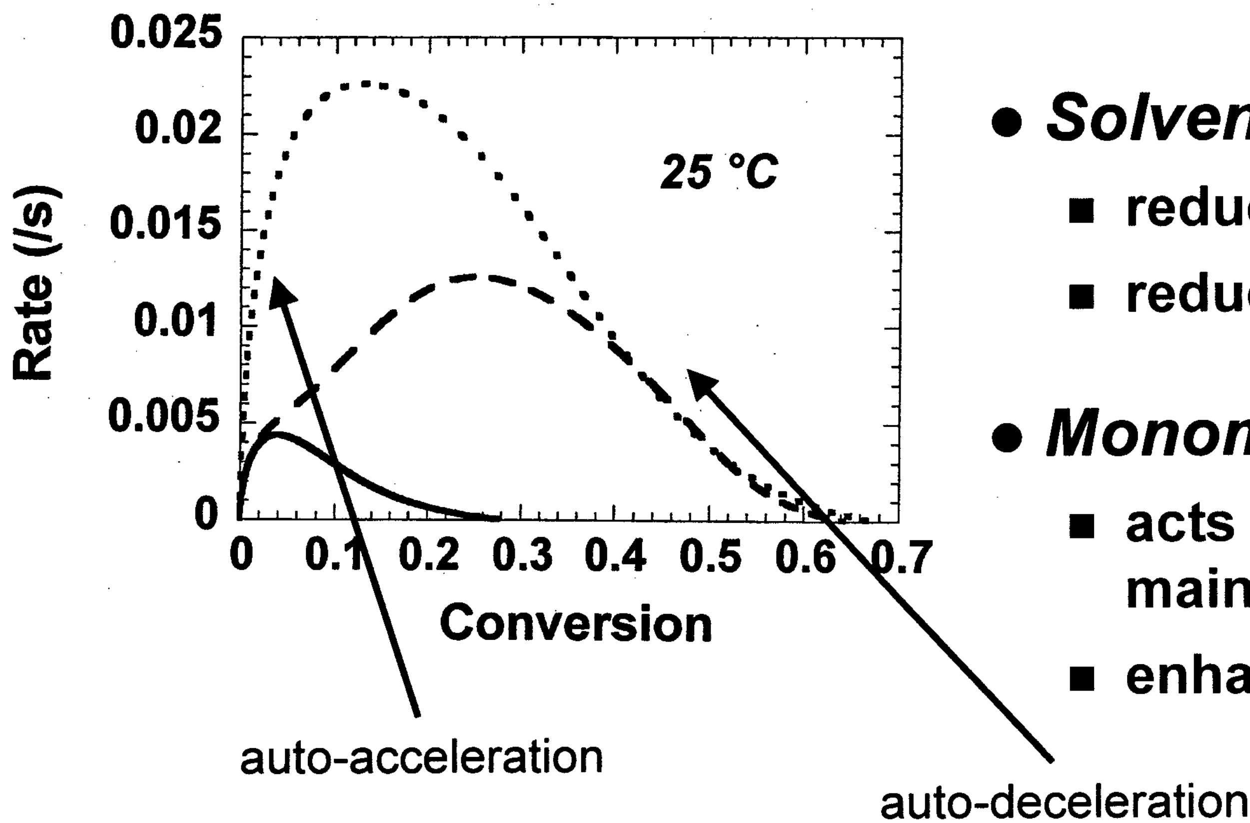
- ***Solvent***
  - *trichloroethylene (TCE)*



Reaction Kinetics

- Radical Formation blue
  $$PI \xrightarrow{k_d} 2I\cdot$$
- Initiation
  $$I\cdot + M \xrightarrow{k_i} IM\cdot$$
- Propagation
  $$IM\cdot + M_n \xrightarrow{k_p} IM_{n+1}\cdot$$
- Termination
  $$IM_m\cdot + \cdot IM_n \xrightarrow{k_t} IM_{m+n}I$$
- Oxygen Scavenging
  $$R\cdot + O_2 \xrightarrow{k_o} ROO\cdot$$

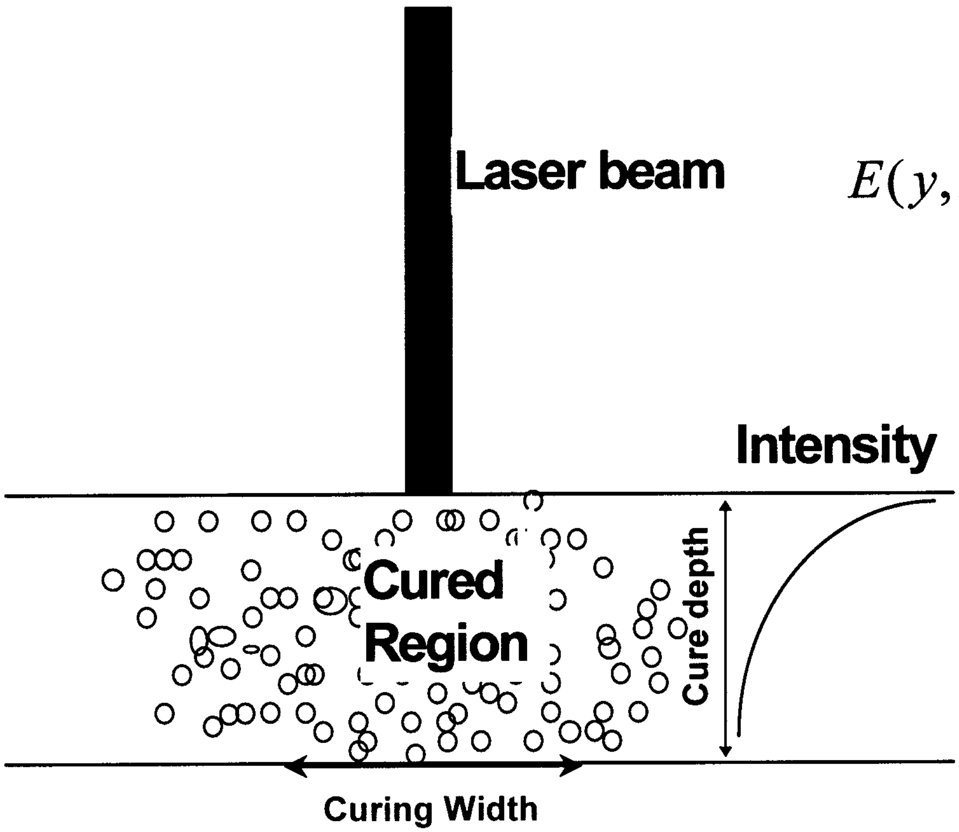
Solvent Versus Reactive Monomer Diluent



- ***Solvent dilution***
  - reduces initial reaction
  - reduces auto-deceleration
- ***Monomer dilution***
  - acts as co-reactant with main monomer
  - enhances auto-acceleration

Data: (-) 100% BisGMA, (--) 100% TEGDMA, (• •) 50/50 BisGMA/TEGDMA; Lovell, et al. *J. of Dental Research.*

Curing Physics



- ***Energy Dosage***

$$E(y,z) = \sqrt{\frac{2}{\pi}}\left(\frac{P_l}{\omega V_s}\right)\exp\left(-\frac{2y^2}{\omega^2}\right)\exp\left(-\frac{z}{D_p}\right)$$

- ***Beer Lambert Law***

$$D_p = \frac{log\left(\frac{I_o}{I_t}\right)}{\varepsilon[PI]}$$

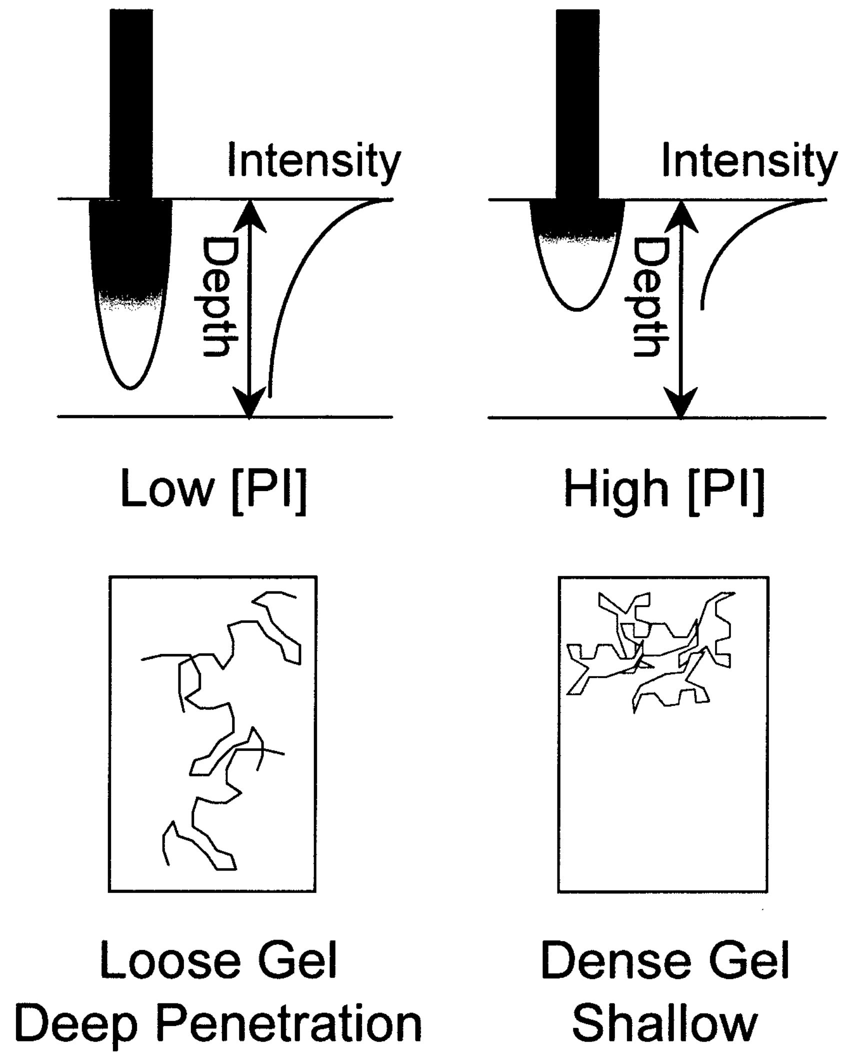
- ***Cure Depth Profile***

$$C_d = D_p ln\left(\frac{E_{max}}{E_c}\right)$$

Department of Chemical Engineering and Princeton Materials Institute
Princeton University

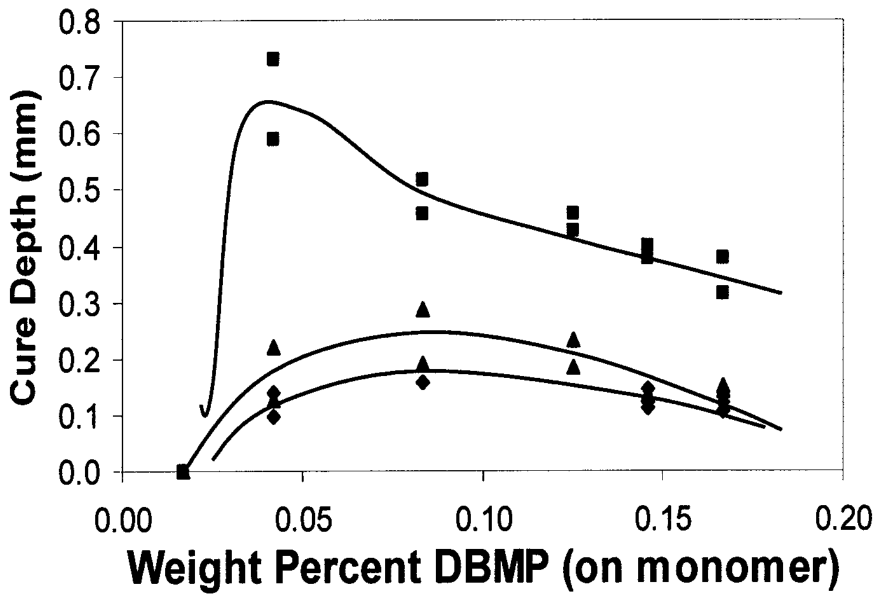
Effect of Photoinitiator Concentration

- ***Photoinitiator absorbs light and decreases laser penetration depth***
- ***Radical formation proportional to laser intensity***
- ***Polymerization & gelation proportional to radical concentration***
- ***BALANCE:***
  - **Depth of Cure**
  - **Polymer Solids Formation**

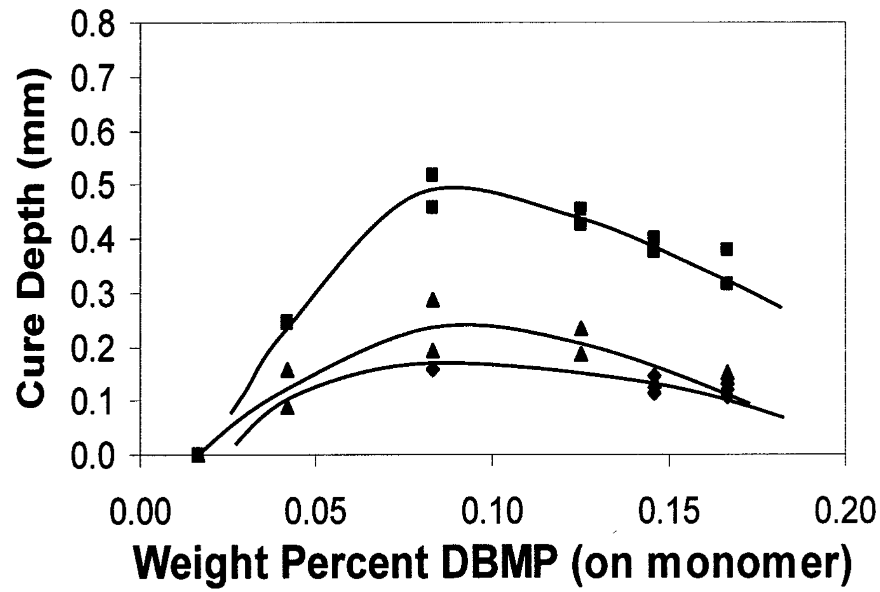


Curing Depth Versus Photoinitiator Concentration

Wet Gel Thickness

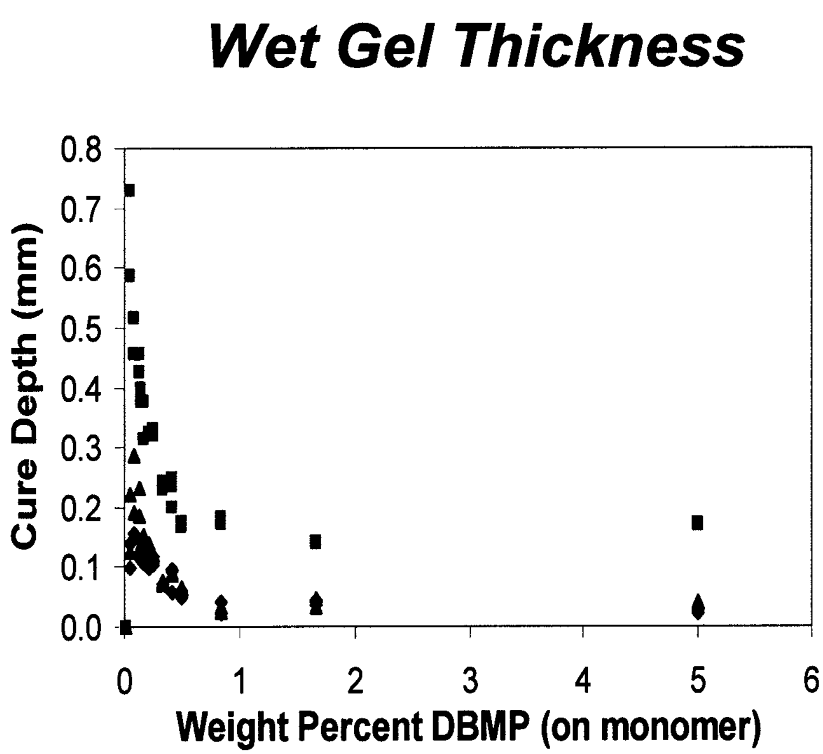


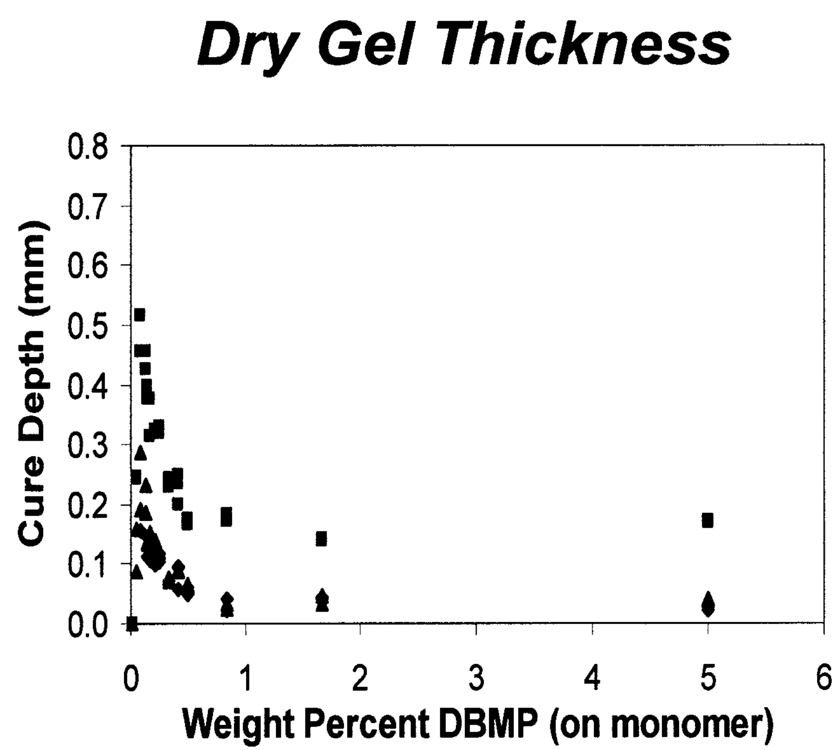
Dry Gel Thickness



Department of Chemical Engineering and Princeton Materials Institute
Princeton University

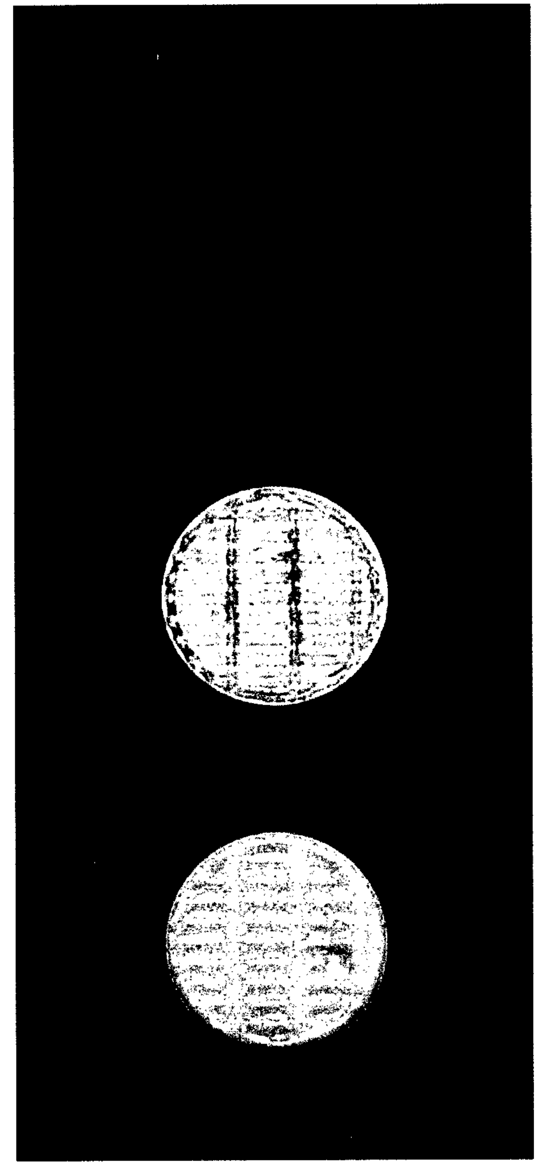
Curing Depth Versus Photoinitiator Concentration (extended data)





Samples

- *Design file:*
  - 1 cm x-y diameter
  - 250 μm z-directional thickness
- *Single-layer BisGMA polymer*
- *Single-layer BisGMA and alumina composite*

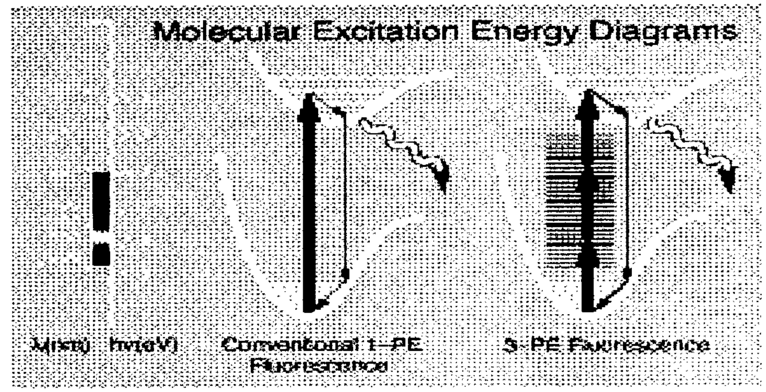


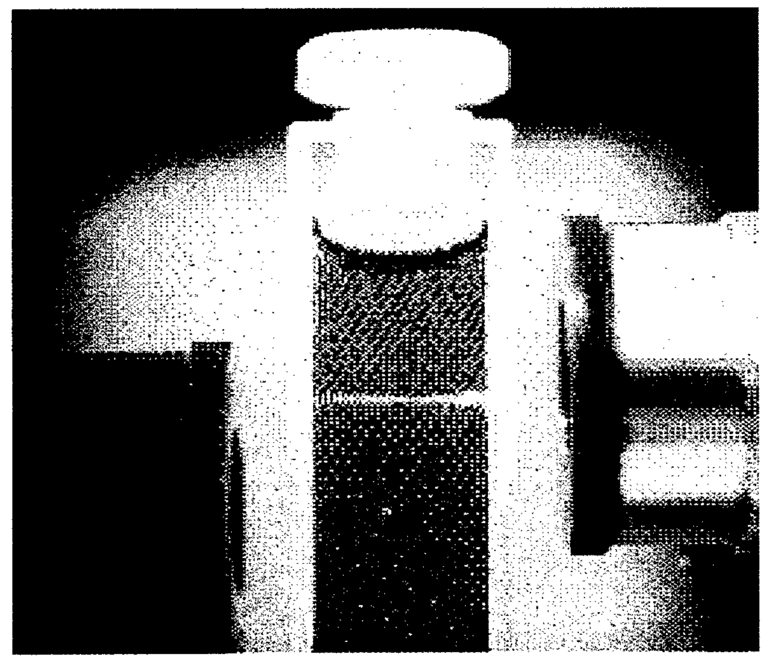
Future Work

- *Fabrication of 3-D materials*
- *Post Curing*
- *Solvent Removal*
- *Mechanical Properties Testing*

2-Photon Excitation Stereolithography

- *Technique from biophysics for fluorescence imaging*
- *Excitation only in regions of multiple photon excitation*
- *Dimensions of O(μm)*
- *Deep penetration*





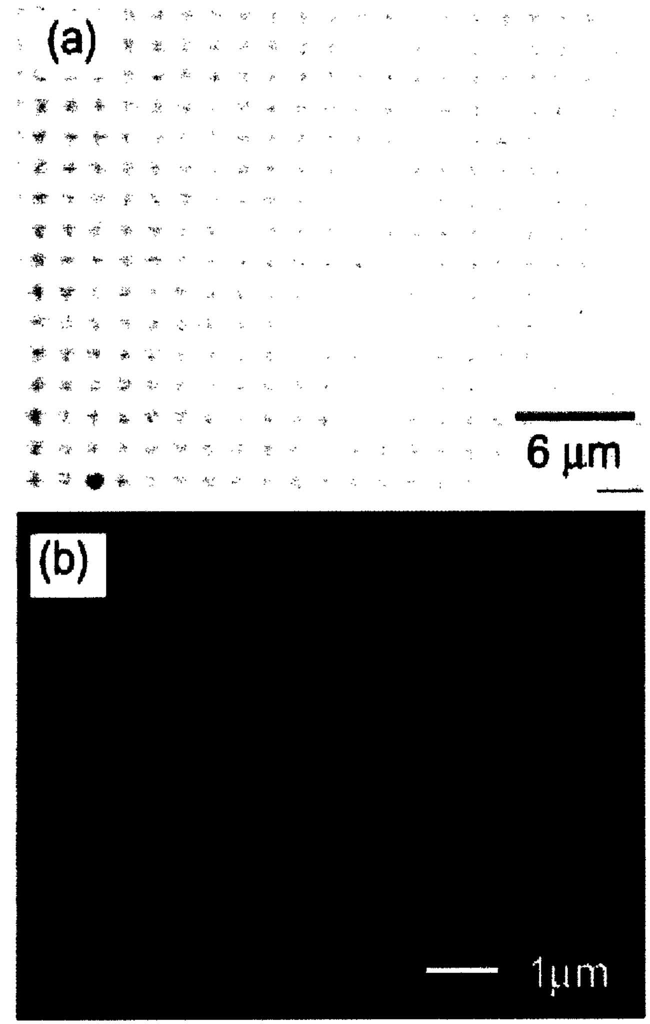
2-Photon Stereolithography

Sun et al. *App Phys Ltrs* **74** 786 (1999)

3D pattern formation for photonic band gap structures

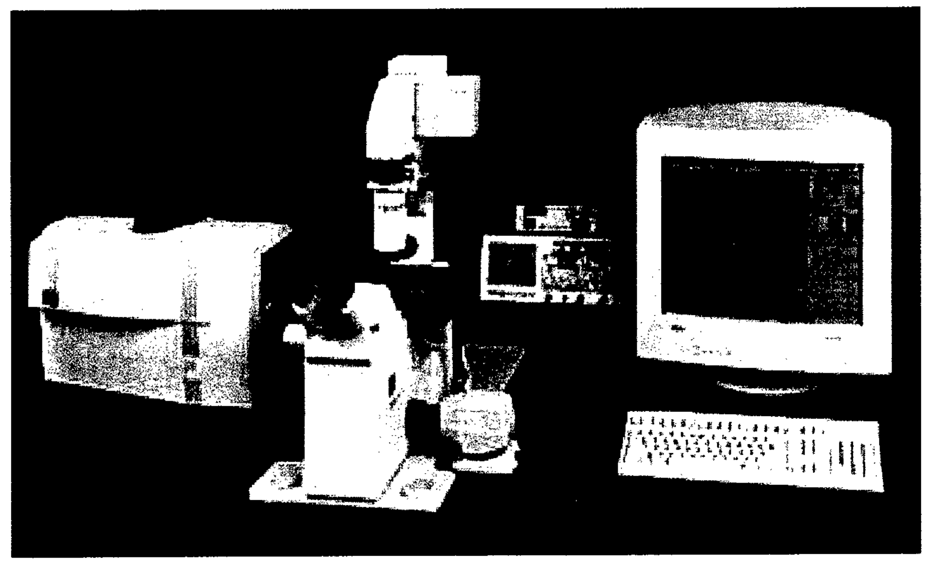
- ***Acrylate resin***
- ***3D translation with piezo transducer***
- ***1 micron features***

Continuation for ceramic materials



2-Photon Instrumentation

- *Long wavelength light (700-1000nm) -non destructive single photon interactions*
- *Low scattering - deep penetration ~ λ^4*
- *Femtosecond pulsed laser*
- *Bio-Rad, Leica,TILL*



Conclusions
Advanced Stereolithography

- *Polymer/Ceramic Stereolithography fundamentals*
  - Curing profiles for composites
  - Post curing densification
- *3D micro Stereolithography*
  - 2-photon instrumentation (purchase with ARO funds)
  - Extension to ceramics and ceramic composites

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Mesoscopic Composites as Small Materials Systems

GEORGE M. WHITESIDES

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CAMBRIDGE, MASSACHUSETTS 02138

FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

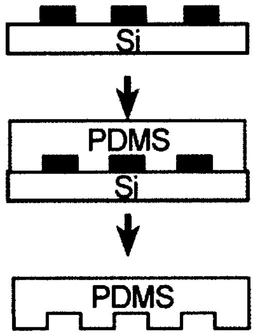
SEPTEMBER 28 - 29, 1999

MURI Program Review
Harvard University
September 28, 1999

Agenda for Whitesides Group Presentation

Introduction	George Wh
Soft Lithography	Kateri Paul
Rapid Prototyping using Soft Lithography	Tao Deng
Methods for the fabrication of small, functional structures	
Metals:	
Microorigami	Scott Brittai
Trusses	Scott Brittai
Slot Filters	Kateri Paul
Heat Exchangers	Francisco A
Composites	Francisco A
Self-Assembly of 3D Circuits	David Graci
Microcontact Printing on Curved Surfaces	Hongkai Wu
Microfabrication of Complex Geometries	Hongkai Wu
FLO for Fabrication of Microelectrode Systems	Paul Kenis
Ceramics, etc.:	
C/Si	Scott Brittai
Si/B/C/N	Hong Yang
General Methods	
Metals:	
Microelectrochemistry:	
Applications for non-planar surfaces	Scott Brittai
Rapid Prototyping Using Silver Halide Film	Tao Deng
3D Microfabrication in Microfluidic Systems	Janelle And
Self-Assembly of Microstructures	Tom Clark
Polymers:	
Dali Crosses	Hong Yang
Future Directions	Kateri Paul

Techniques of Soft Lithography

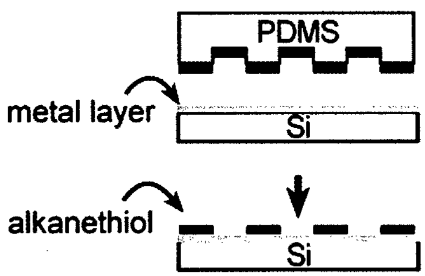


Master: prepared by photolithography, micromolding, or other techniques

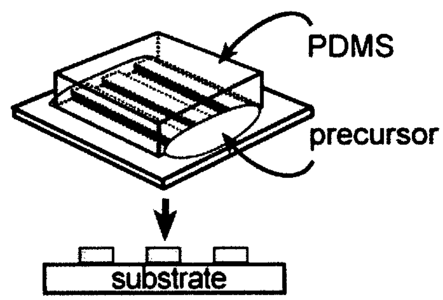
Pour prepolymer and cure

Remove stamp

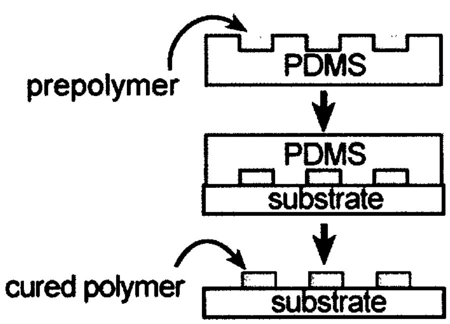
Microcontact printing



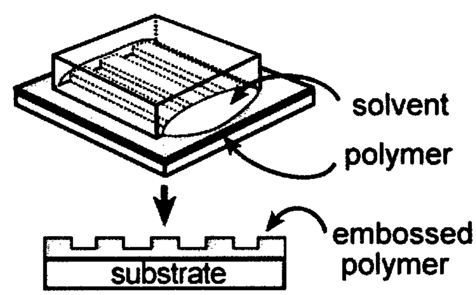
Micromolding in capillaries



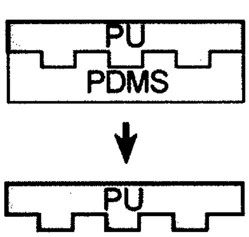
Microtransfer molding



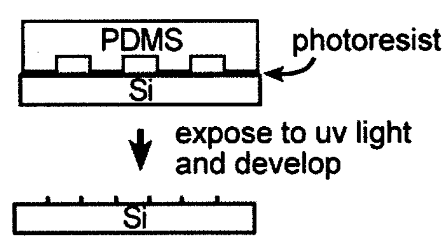
Solvent-assisted Embossing



Replica molding



Near field lithography



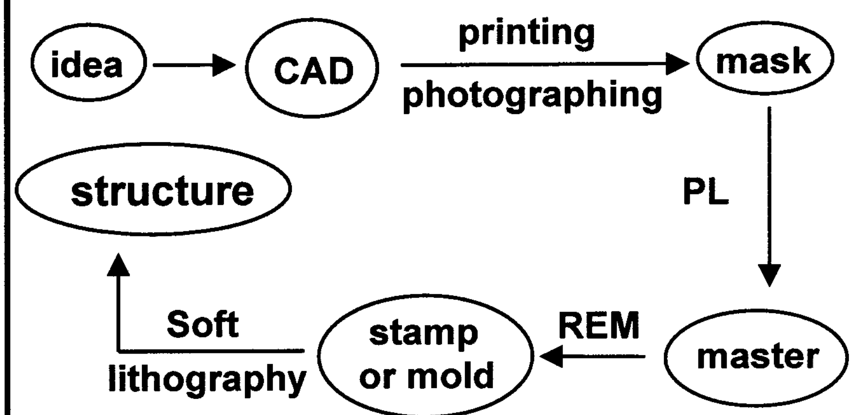
Rapid Prototyping Using Soft Lithography

Tao Deng, Dong Qin, and George M. Whitesides
Department of Chemistry, Harvard University

Objective

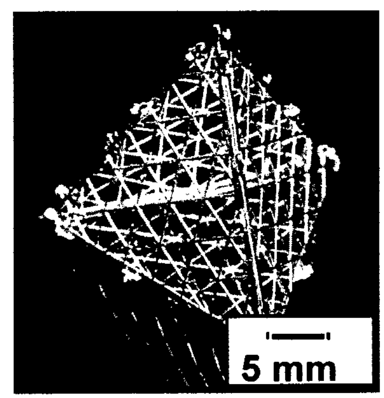
Development of new methods and materials for rapid prototyping of microstructures for chemistry, biology and materials laboratories

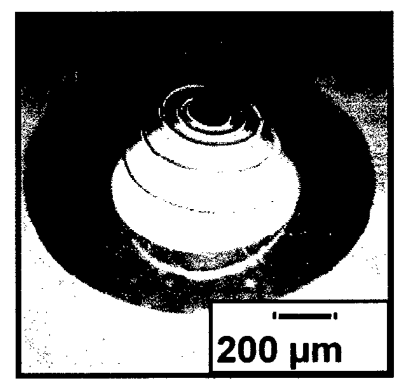
Technical Approaches



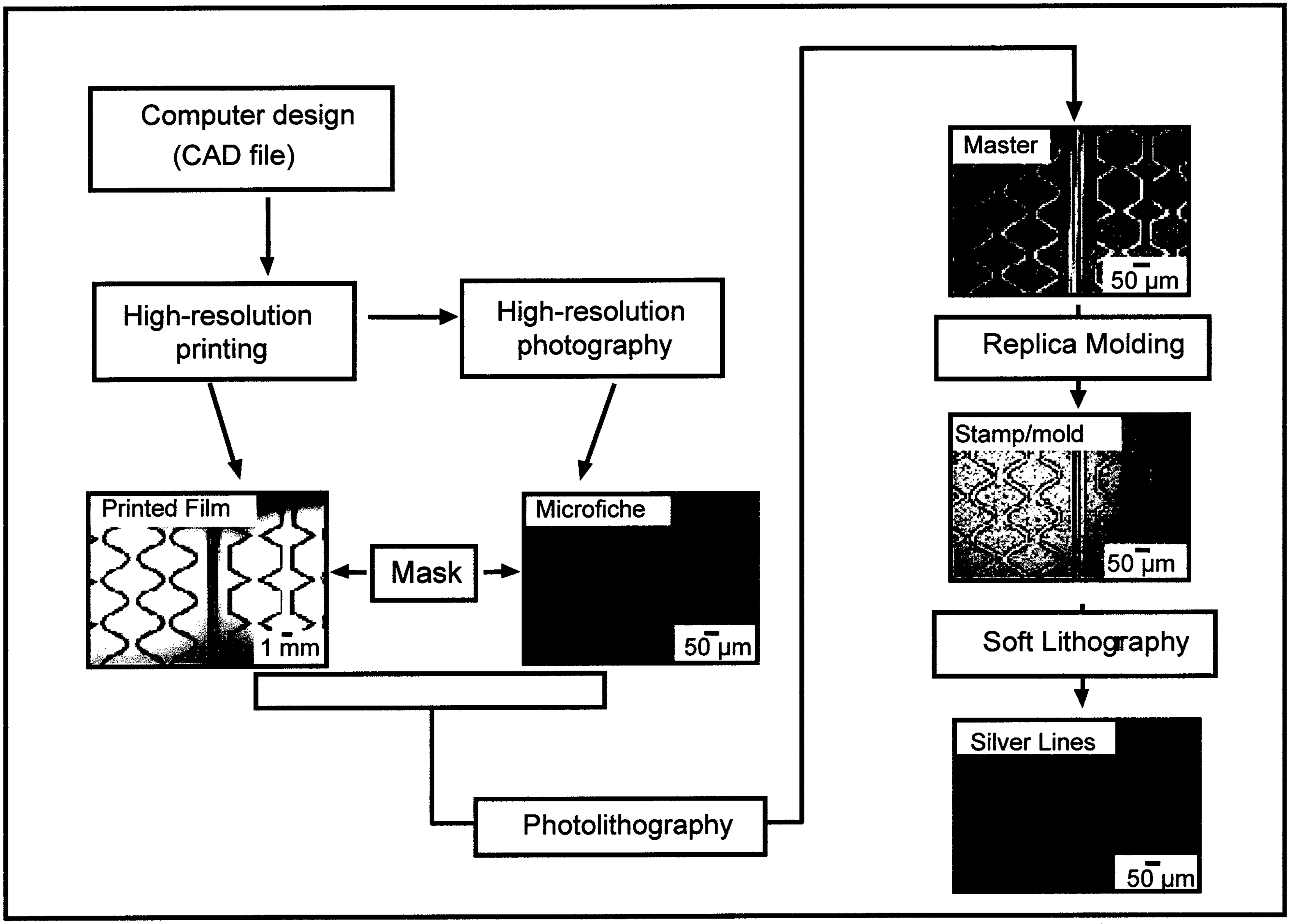
Accomplishments

- Rapid prototyping complex microstructures (>20 μm) using printed film
- Rapid prototyping complex microstructures (>10 μm) using microfiche





Process for Rapid Prototyping using Soft Lithography



T. Deng, J. Tien, B. Xu, and G. M. Whitesides

Microelectrochemistry: Microorigami

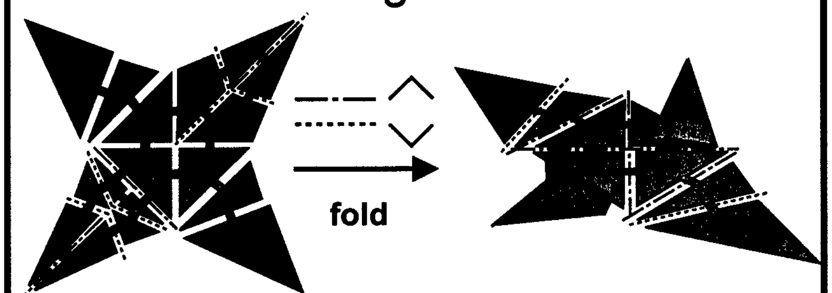
Scott T. Brittain, Olivier Schueller, Hongkai Wu, Sue Whitesides (McGill), George M. Whitesides, Harvard University

Objectives

- To fabricate complex, 3D structures in metals for potential use in MEMS, microrobotics, UAVs, microsatellites

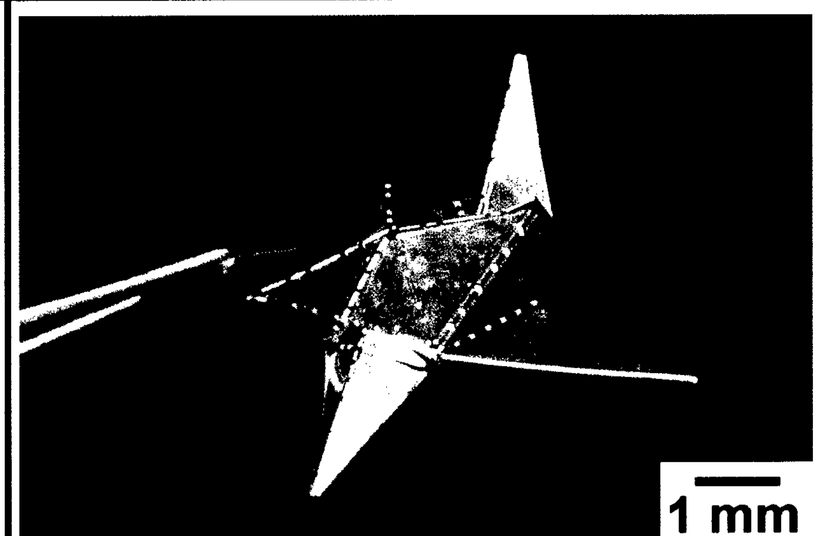
Technical Approach

- μCP, wet etching, electroplating, manual folding



Accomplishments

- 3D metallic structures fabricated from single layer, 2D patterning technique
- Topographical transformations
- sub-mm feature sizes



Microelectrochemistry: Trussed Structures

Scott T. Brittain, Olivier Schueller, Yuki Sugimura, Anthony G. Evans, George M. Whitesides, Harvard University

Objectives

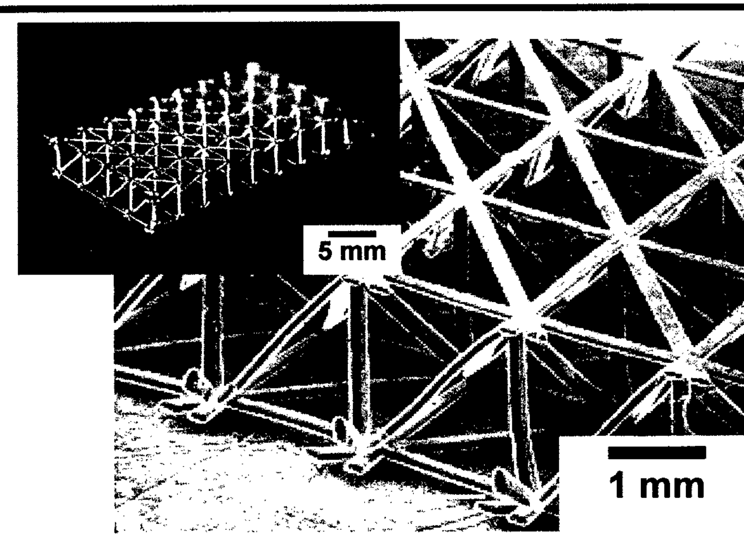
- To fabricate complex, 3D structural elements in metals for potential use in MEMS, microrobotics, UAVs, microsatellites

Technical Approach

- Microcontact Printing (μCP)
- Wet chemical etching
- Electroplating
- Manual assembly
- Electrochemical welding

Accomplishments

- Truly 3D metallic structures
- cm-scale objects with mm-scale structural repeats and ~100 μm feature sizes
- multilevel registration to 100 μm

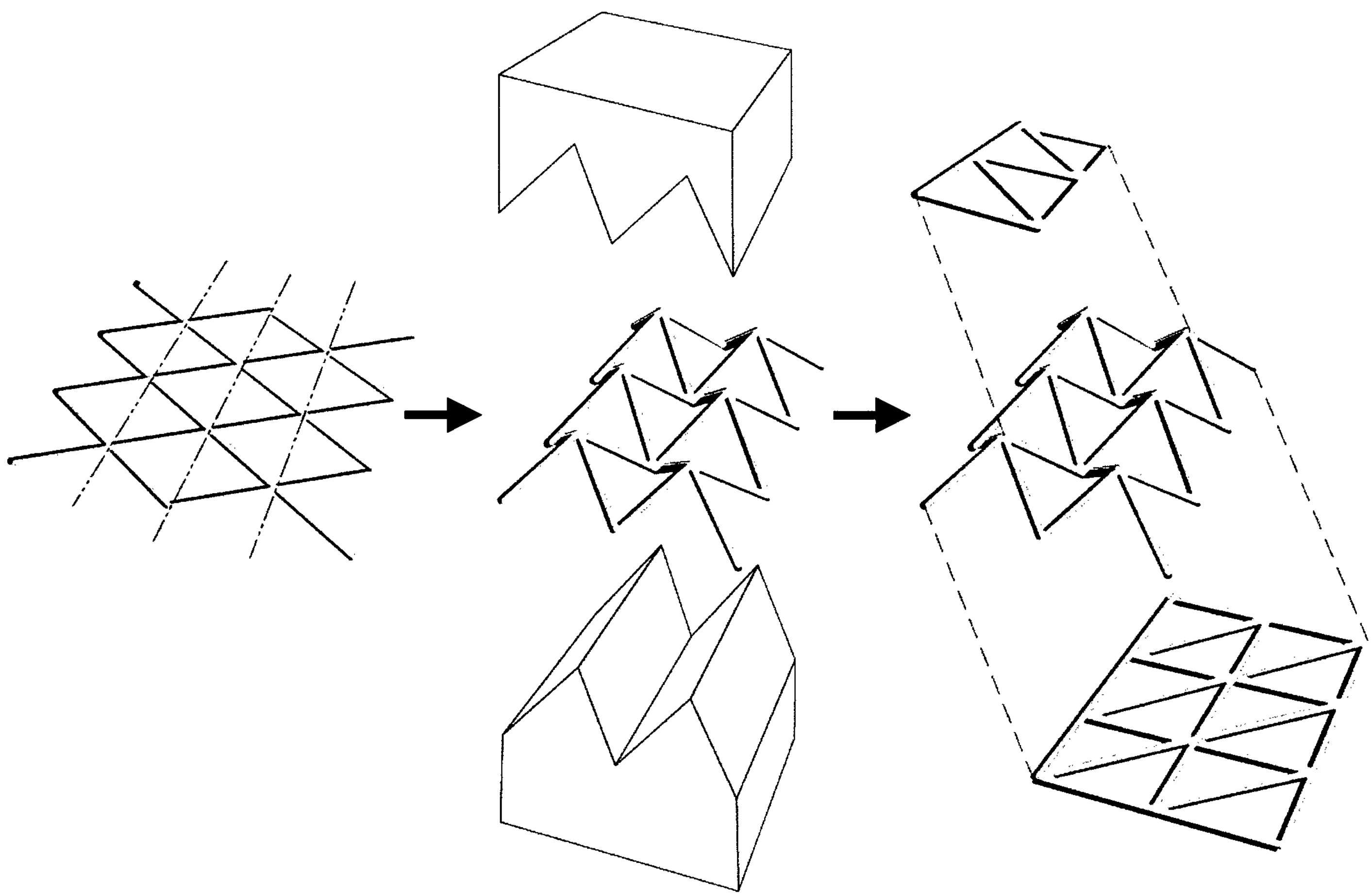


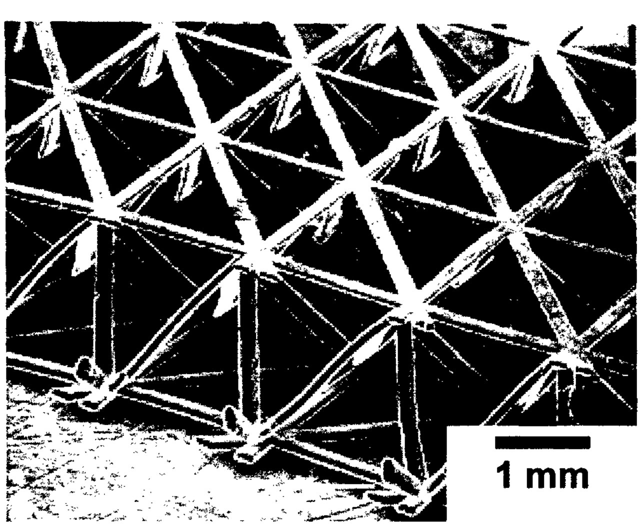
Fabrication of Microtruss

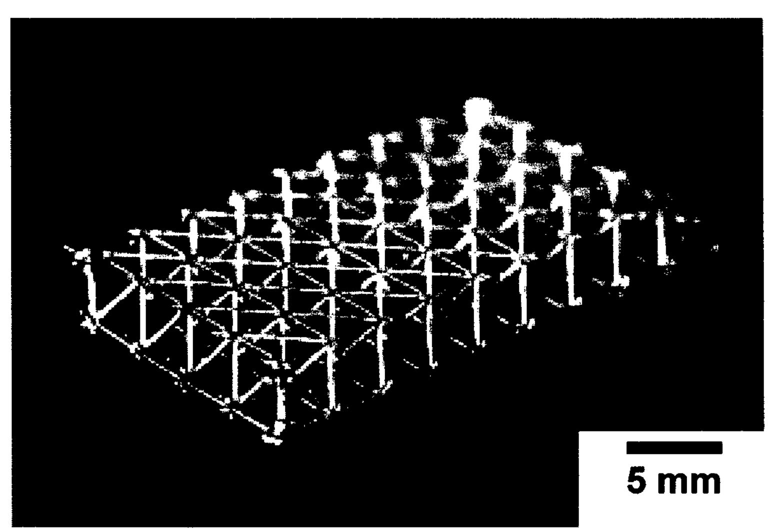
Fabricate planar Ag grid using µCP and electroplating.

Fold 70 deg along axes using tweezers and brass die.

1. Assemble by Hand.
2. Affix corners with Ag paint.
3. Electroplate Ni.







Topographically Directed Photolithography: Photoresist as its Own Optical Element

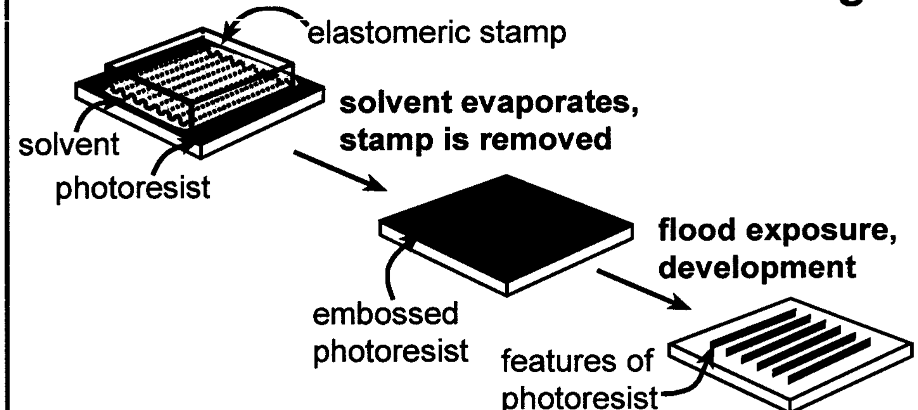
Kateri E. Paul, Tricia L. Breen, Joanna Aizenberg and George M. Whitesides
Department of Chemistry and Chemical Biology, Harvard University

Objective:

Generate < 100-nm features over a large area using an unconventional photolithographic technique: maskless lithography.

Technical Approach:

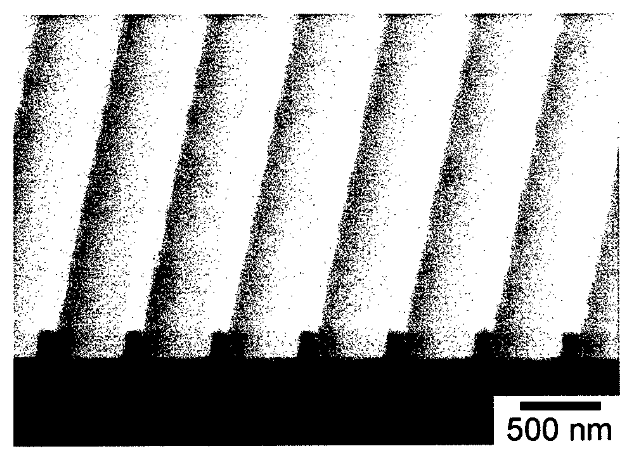
Solvent Assisted Embossing



Accomplishments:

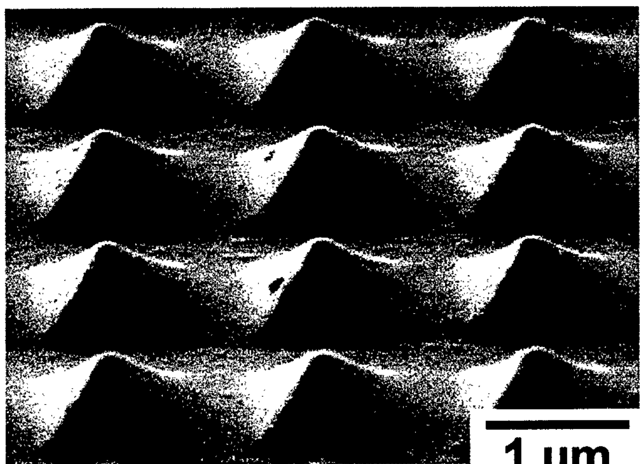
- Features as small as ~ 70 nm, with a period of ~400 nm, generated in photoresist on silicon
- Reactive ion etching (RIE) and lift-off transfer features to the substrate
- Technique can be combined with an amplitude mask to generate more complex structures
- Areas of ~8 cm^2 patterned

~70 lines produced by a sinusoidal grating

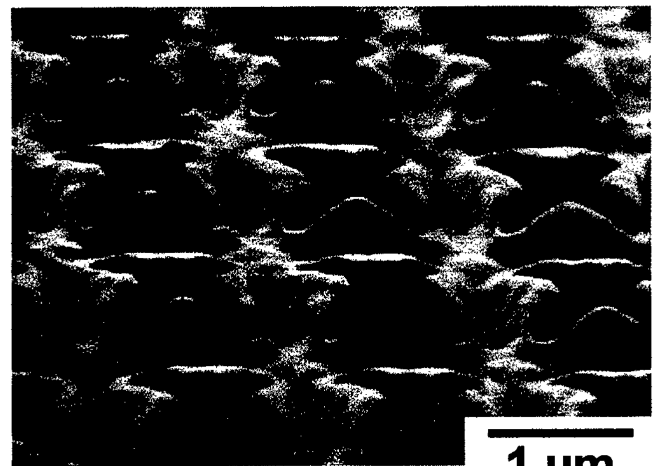


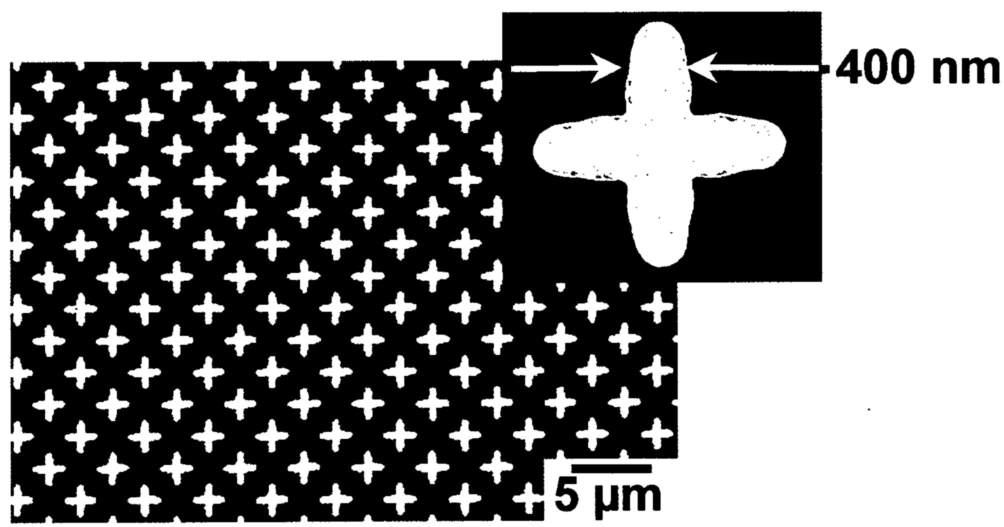
Topographically Directed Photolithography: generation of a dipole array

Embossed photoresist



Exposed photoresist





Lift-off; gold on silicon

Fabrication of Metallic Heat Exchangers Using Sacrificial Polymer Mandrils

*Francisco Arias, Scott Oliver, Bing Xu, and George M. Whitesides**
Department of Chemistry, Harvard University

Objectives: New processes, use sacrificial polymer frameworks to construct three-dimensional metallic structures.

Applications: Cooling systems for electronic components and diffraction gratings.

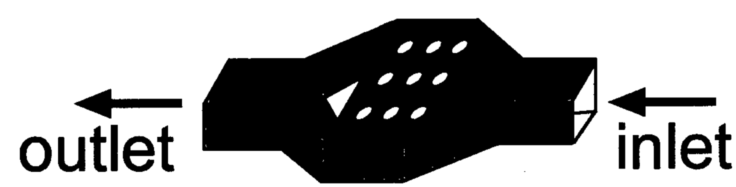
Technical Approach:

- Rapid prototyping
- Microtransfer molding
- Vapor deposition
- Electroplating

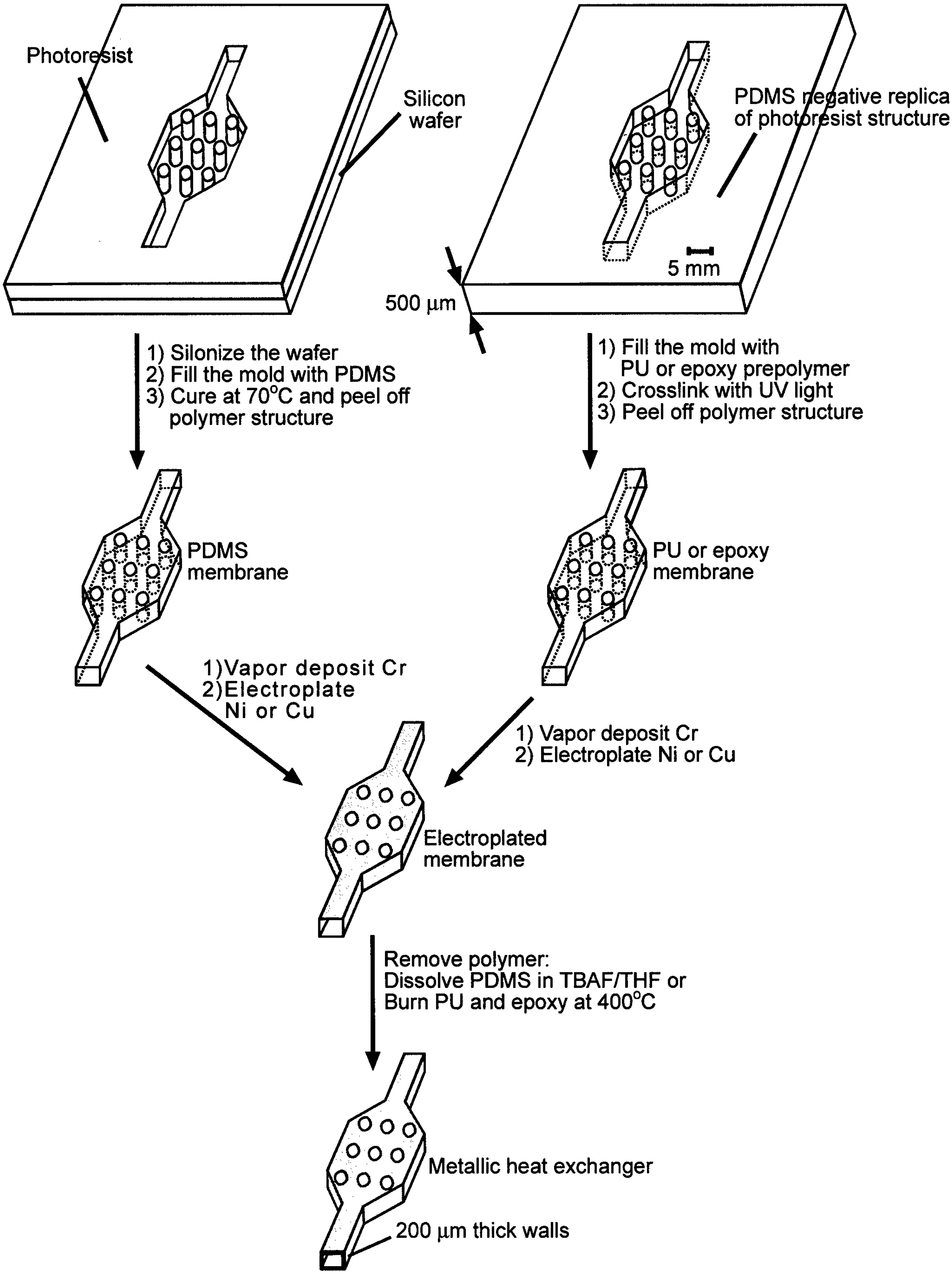
Accomplishments:

- Fabricated nickel thermal modules with 200-500 μm wide channels.
- We are able to prepare heat exchangers with various features: 400-200 μm unfilled cylinders, 500 μm stripes, or 150 μm posts.

Heat Exchanger Design

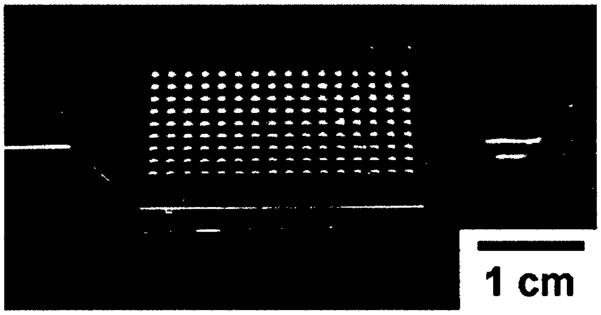


Fabrication of Heat Exchangers

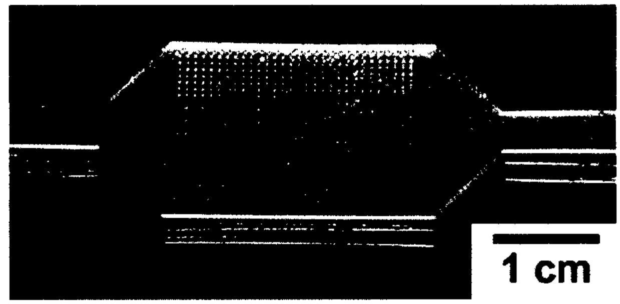


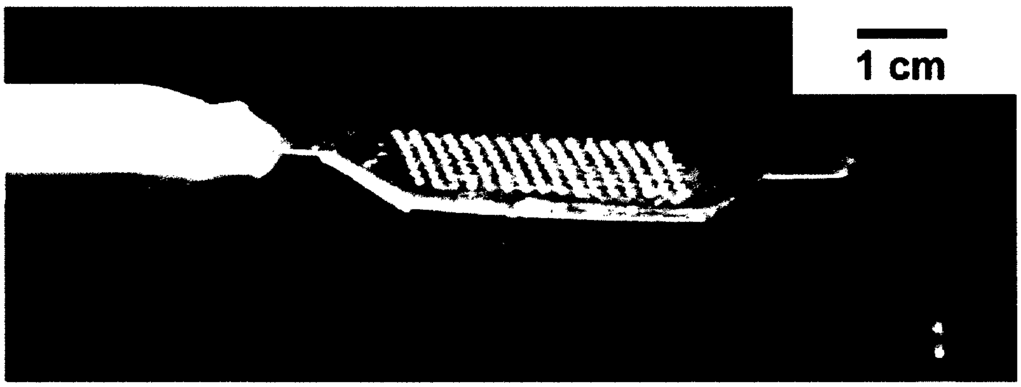
Characterization of Heat Exchangers

400 μm unfilled cylinders

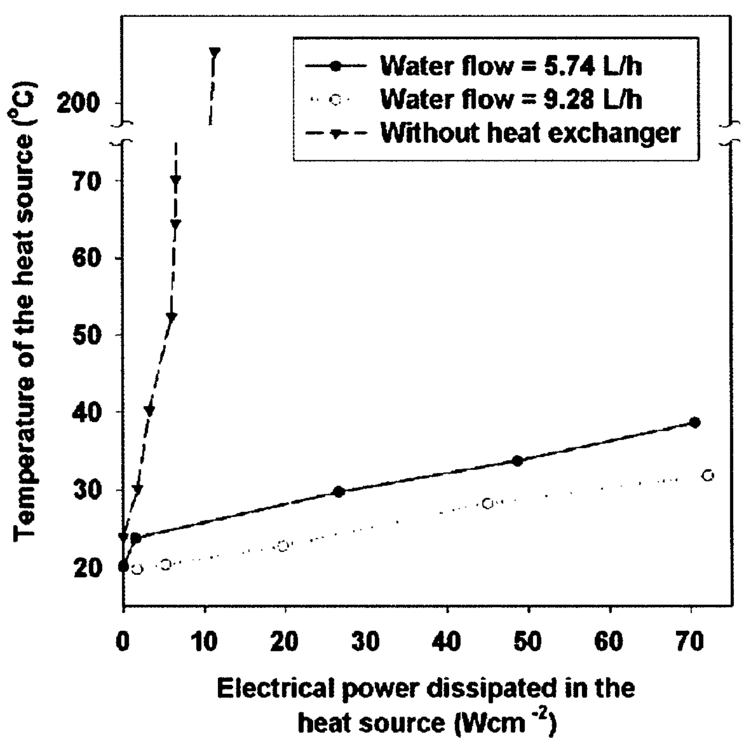


150 μm posts





Performance of nickel specimen with 400 μm unfilled cylinders



Microscale Sandwich Panels

Francisco Arias, Bing Xu, George M. Whitesides, Yuki Sugimura, Anthony Evans**
Department of Chemistry, Harvard University

Objectives: Fabrication of materials with high strength-to-weight ratio and low production cost.

Applications: Hard disk drive arms, small air vehicles, military equipment, hydrophones, and structural biomaterials.

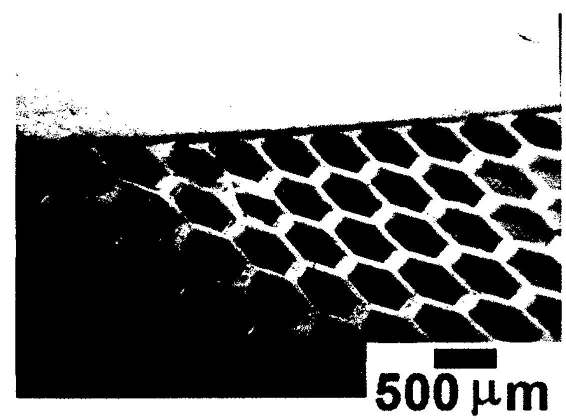
Technical Approach:

- Rapid prototyping
- Microtransfer molding
- Microembossing
- Electroplating
- Pb/Sn Soldering

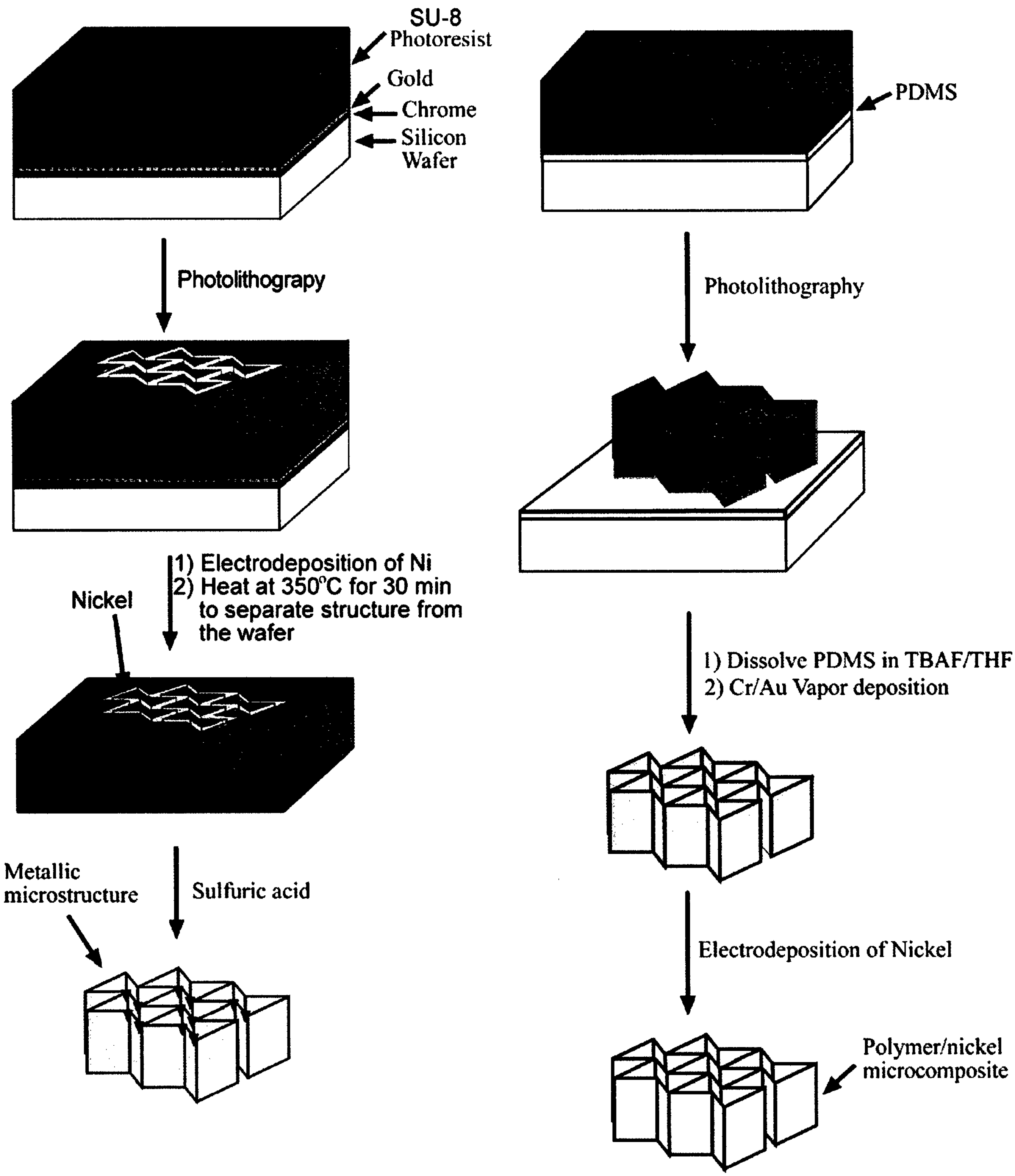
Accomplishments:

- Fabricated metallic and polymeric microgrids with high-aspect-ratio : honeycombs, negative Poisson's ratio, and quasiperiodic patterns.
- Prepared microscale sandwich panels and measured their bending moduli.

Metallic Honeycomb Panel

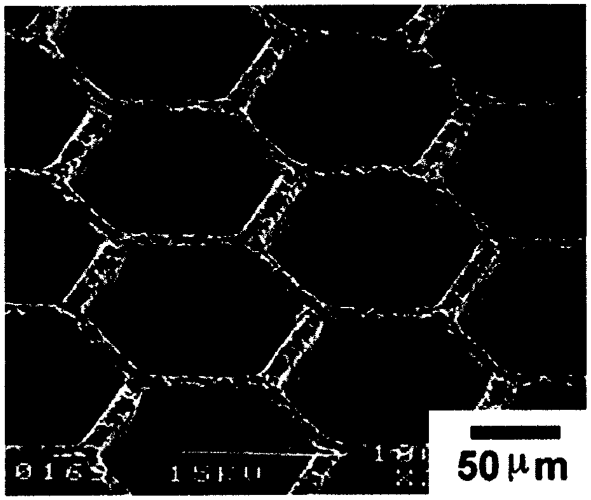


Fabrication of Microgrids

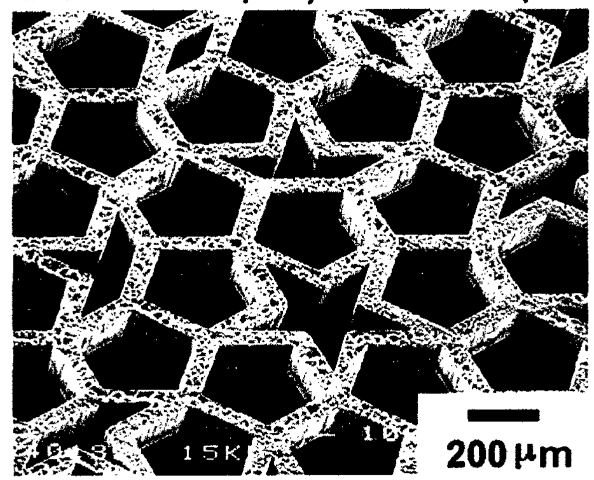


Metallic Microgrids

Honeycombs
Diam = 150 μm; WW = 15 μm

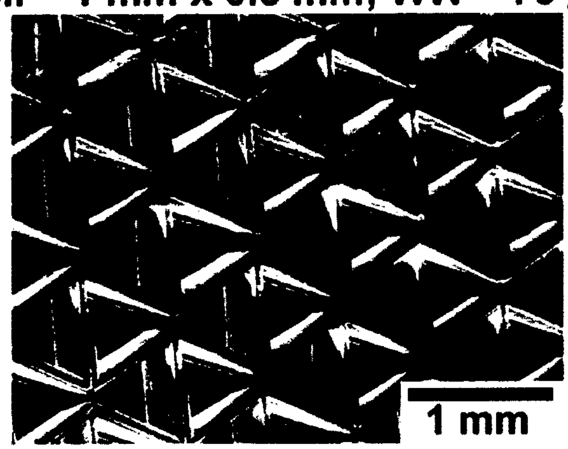


Kemper's pentaling
Diam = 400 μm; WW = 75 μm

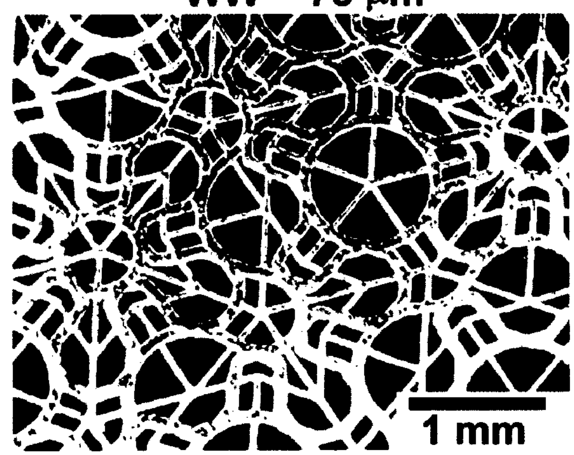


Polymer/Metal Microgrids

NPR structure
Cell = 1 mm x 0.5 mm; WW = 75 μm

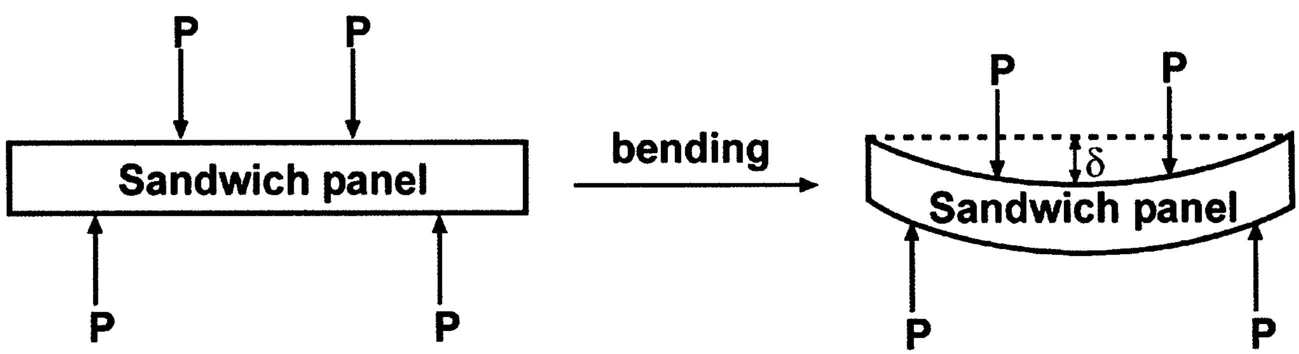


A Penrose's structure
WW = 75 μm



Bending Tests of Sandwich Panels

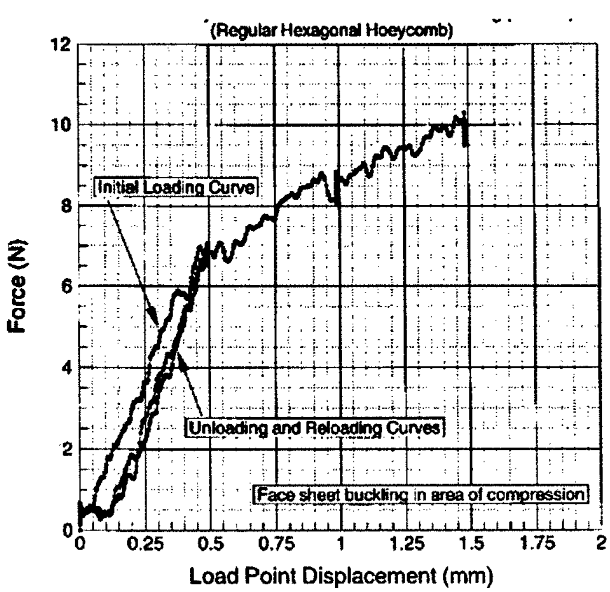
Four-point bending test:



δ = load point displacement

$$\boxed{EI = 6.67 \times 10^{-7}\ P/\delta}$$

Force vs. load displacement plot for a nickel honeycomb panel:



Bending Moduli:

Exp. 136 GPa
Theor. 132 GPa

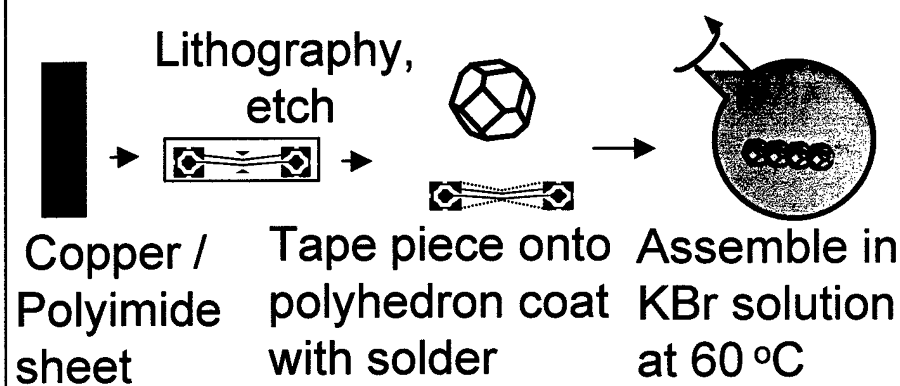
Forming Electrical Networks in Three Dimensions by Self-Assembly

D. H. Gracias, J. Tien, T. L. Breen, C. Hsu and G. M. Whitesides
Department of Chemistry and Chemical Biology, Harvard University

Objectives:

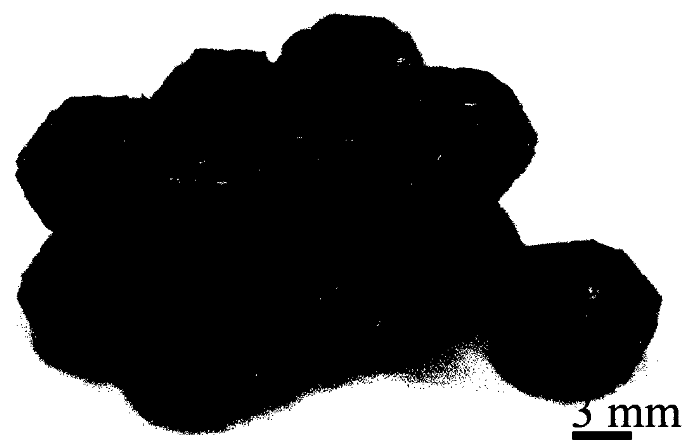
- Demonstrate self-assembly with pin-on-pin electrical contacts.
- Self-assemble electrical networks in three dimensions with local and global connectivity.

Technical Approach:

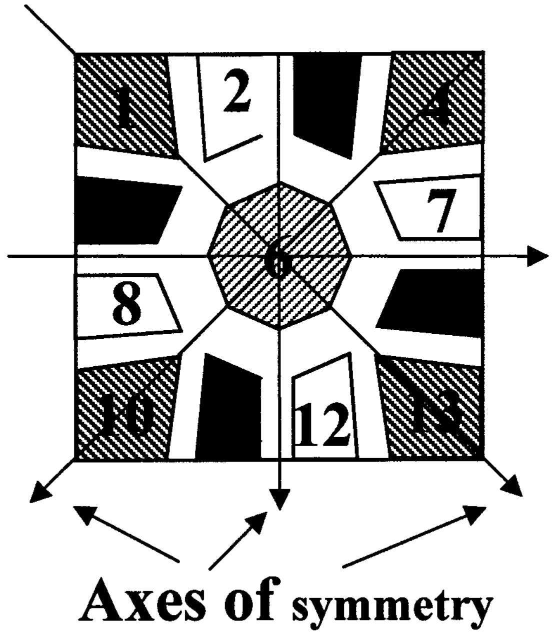


Accomplishments:

- Self-assembled 2x2x3 polyhedra with local and global networks.
- Self-assembled wedge shaped polyhedra to form a solenoid.



Pin-On-Pin Connections and Connectivity

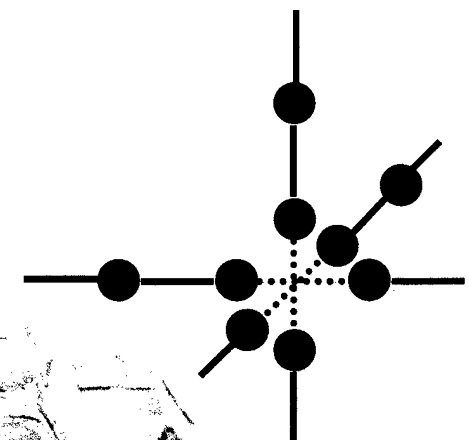


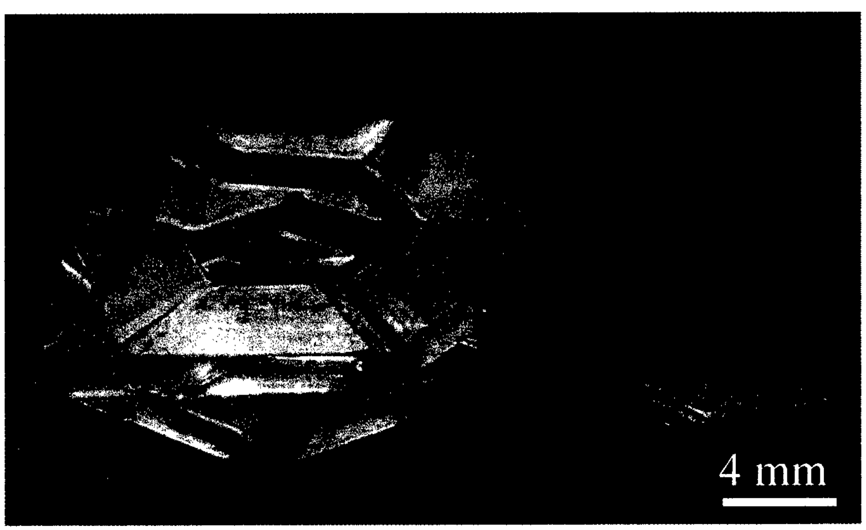
$A_i \Longleftrightarrow A_i$

- 1, 4, 10, 13
- 6

$A_i \Longleftrightarrow A_j$

- 3, 5, 9, 11
- 2, 7, 8, 12





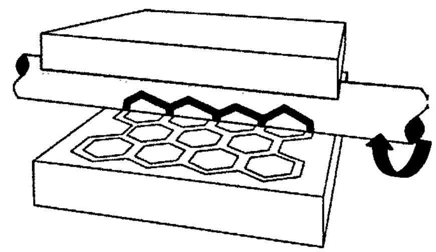
Printing on Curved Surfaces

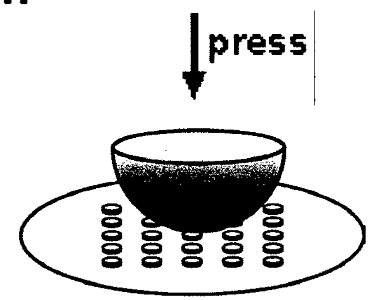
R. Jackman, S. Brittain, H. Wu, G.M. Whitesides,
Department of Chemistry, Harvard University

Objective

- To Pattern curved surfaces
- To fabricate microstructures using the curved surfaces as sacrificial layer

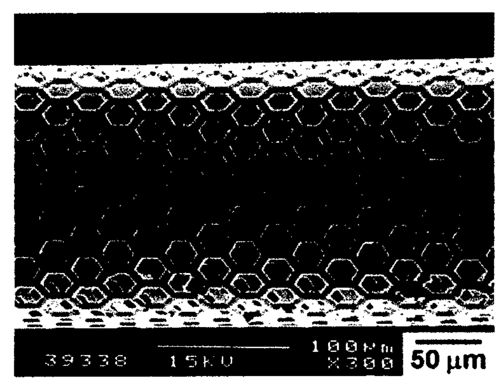
Technical Approach





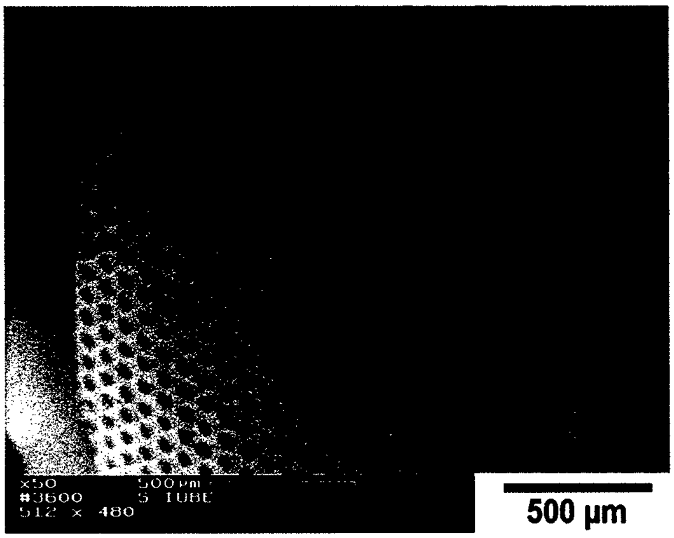
Accomplishments

- Features ≥ 3 μm were printed on cylindrical surfaces (curvature ≥ 100 μm)
- Features ≥ 1 μm were printed on spherical surfaces (curvature ≥ 2 mm, and ≥ 60 degrees of the surface area)

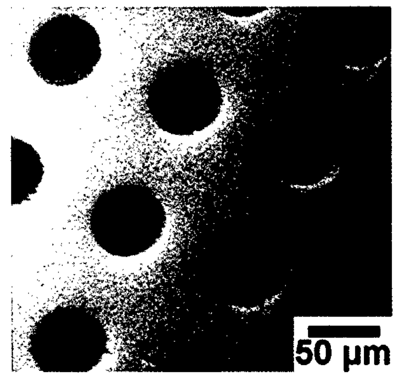


Print on Curved Surfaces

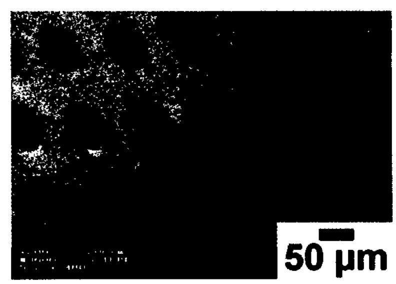
spherical surface

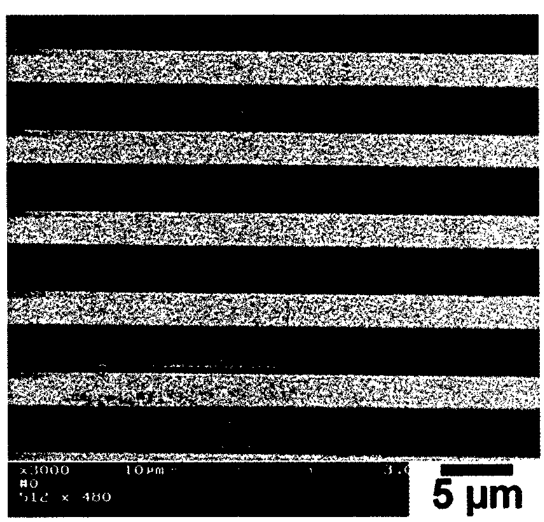


apex



edge





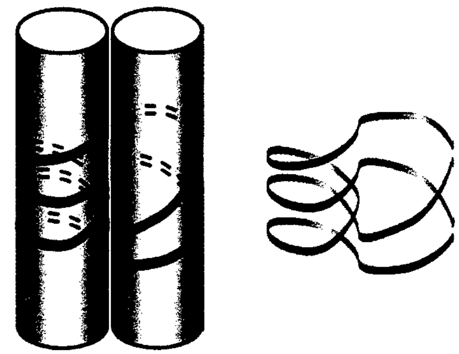
Complex Geometry

Hongkai Wu, Scott Brittain, Bartosz Grzybowski, Prof. Sue Whitesides, Prof. G.M. Whitesides
Department of Chemistry, Harvard University

Objectives

- To fabricate topologically complex three-dimensional objects

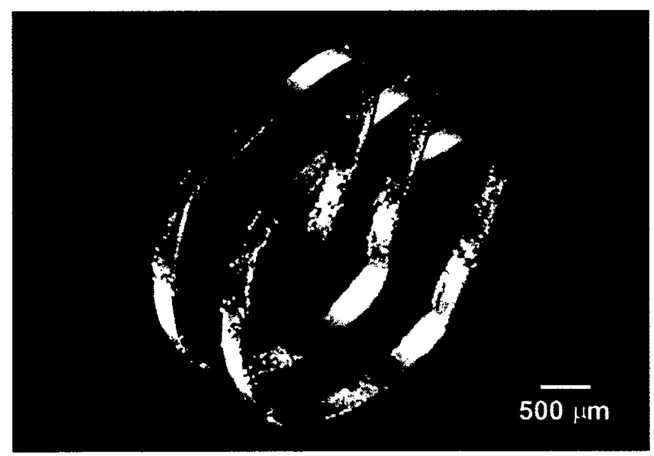
Technical Approach



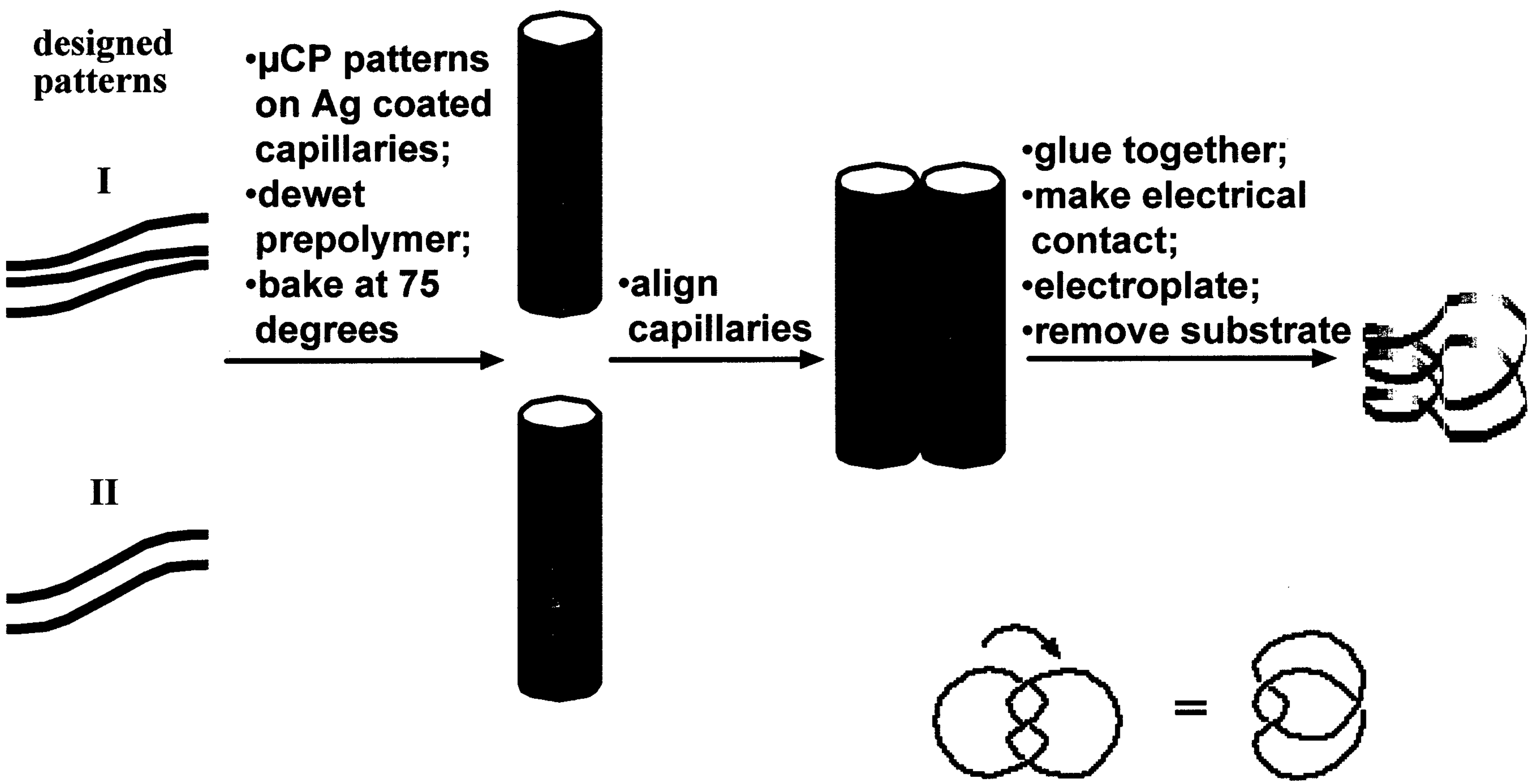
pattern design
photolithography
μcontact print
align
electroplate weld
release

Accomplishment

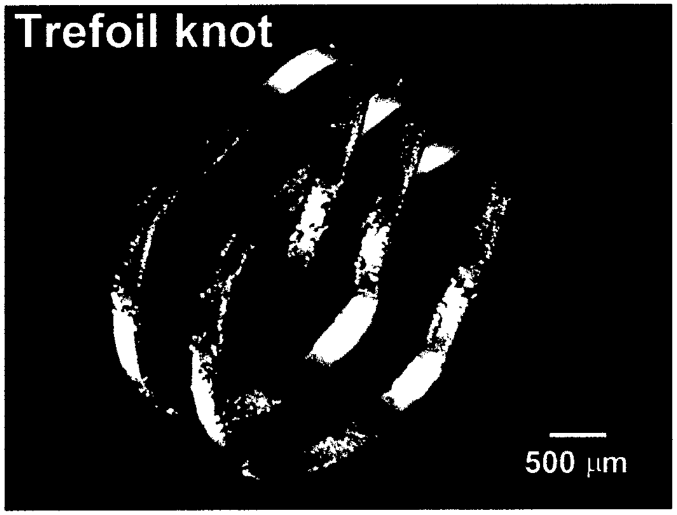
- Increased topological complexity
  — planar design → multiple crossings
- Complex 3D structures
  — knots
  — chains
  — Möbius strip

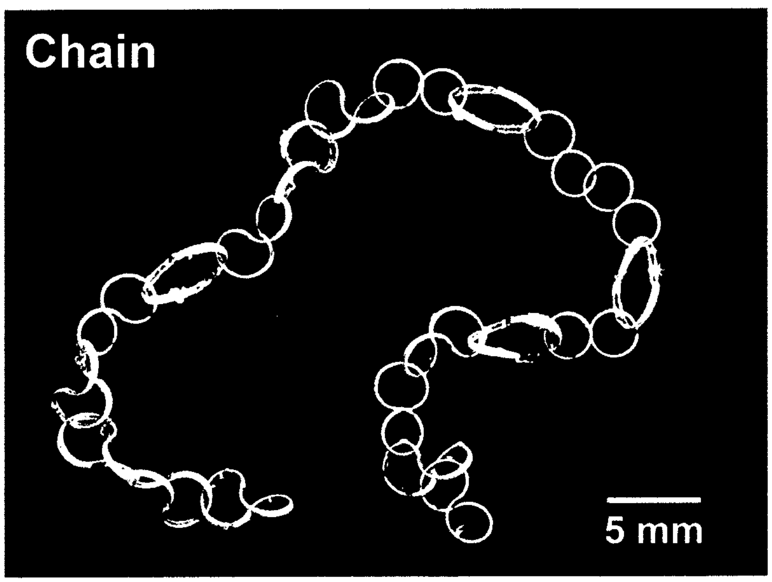


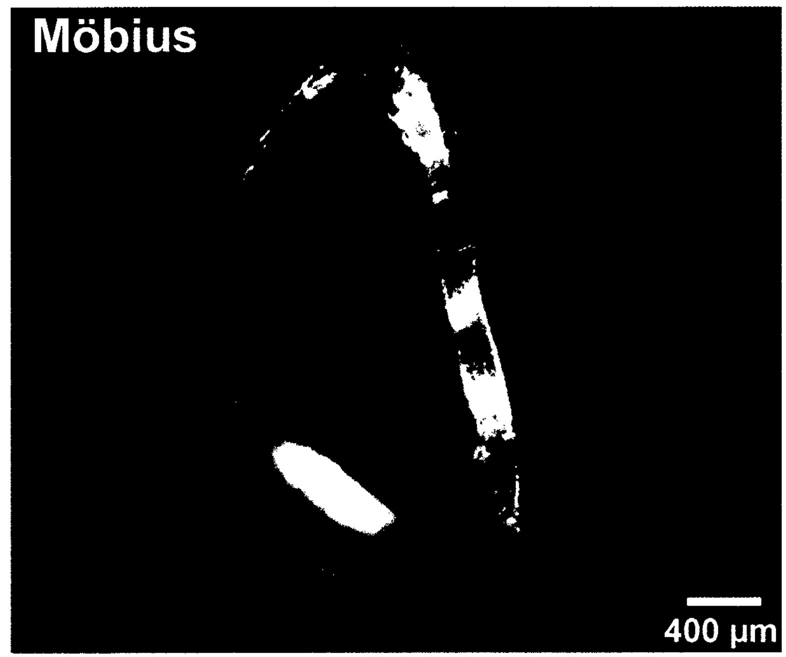
Fabrication of Complex Geometry



Complex Geometry







Fabrication using Laminar Flow

Paul Kenis, Rustem Ismagilov, and George M. Whitesides
Department of Chemistry and Chemical Biology, Harvard University

Objective

Microfabrication inside capillaries (PDMS, glass, composite)

Technical Approach

Apply different chemistries from
- separate flows
- at the interface of flows

using *multiphase laminar flows*

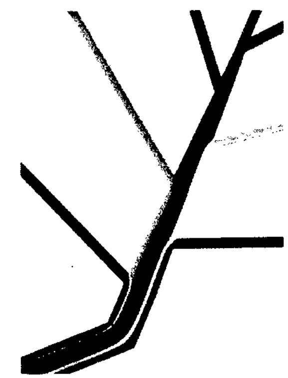


Photo: F. Frankel

Accomplishments

- arrays of crystals
- ridges of polymer
- trenches in SiO_2
- chemiluminescence
- electrode systems

Three-electrode system:

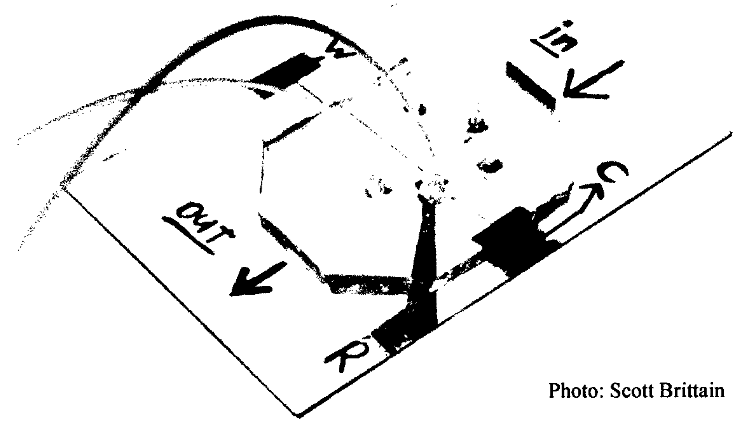
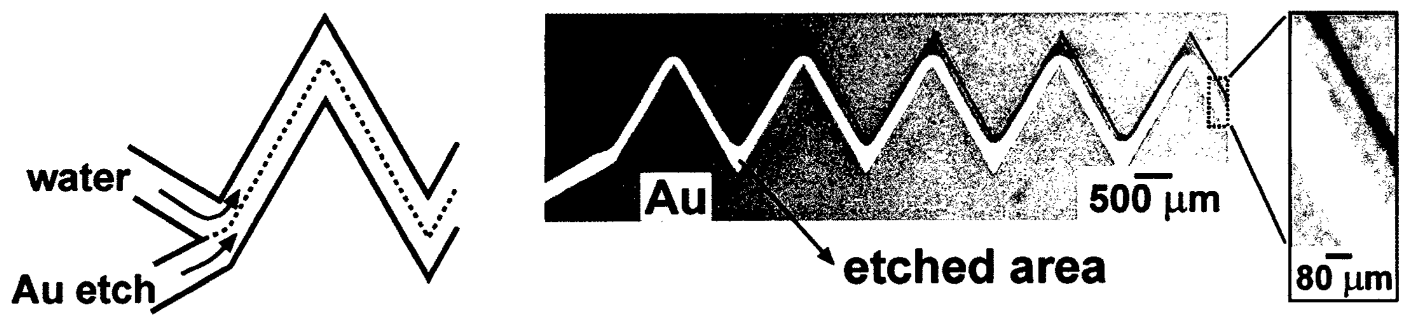


Photo: Scott Brittain

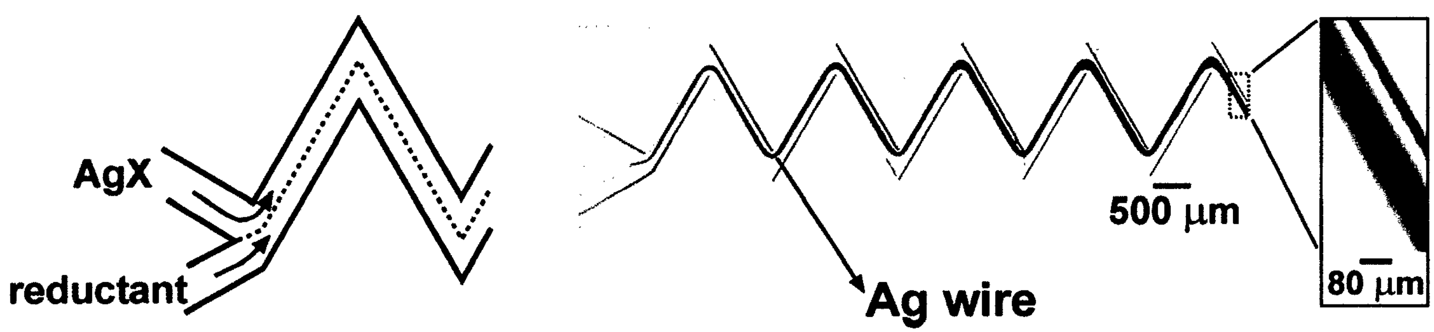
Fabrication using Multiphase Laminar Flow

Apply different chemistries from different phases

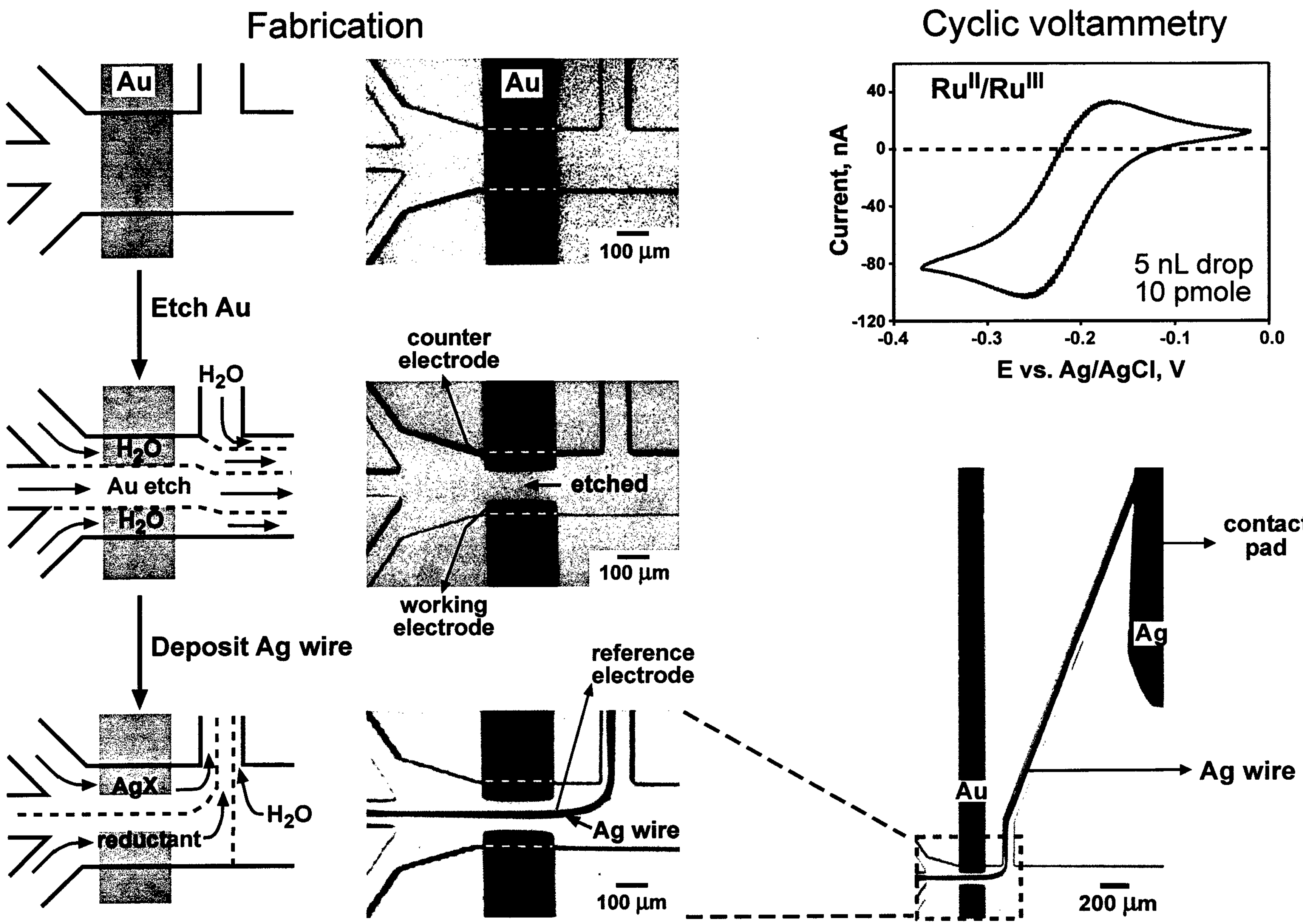
From separate flows



At the interface of flows



In-Channel Three-Electrode System



P.J.A. Kenis, R.F. Ismagilov, G. M. Whitesides, *Science*, **285**, 83-85 (1999)

Ceramics: SiC

Scott T. Brittain, Hong Yang,
George M. Whitesides, Harvard University
Martin Erhardt, Ralph Nuzzo, University of Illinois at UC

Objectives

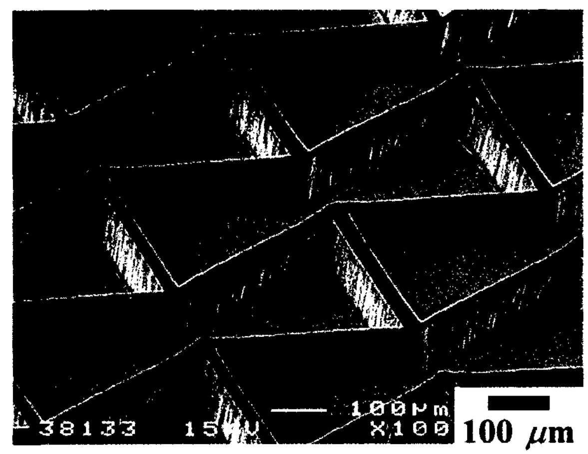
- To coat patterned glassy carbon microstructures with a SiC shell.

Technical Approach

- µTM of precursor to carbon
- pyrolytic conversion to glassy carbon
- vapor deposition of Si
- pyrolytic conversion to SiC

Accomplishments

- Coating of glassy carbon microstructure with 4 µm of Si.



Glassy carbon microstructure before Si deposition.

New Ceramics for the Fabrication of Small Structures

Hong Yang, Scott T. Brittain, Pascal Deschatelets, Robert G. Chapman, and George M. Whitesides
Department of Chemistry & Chemical Biology, Harvard University

Objectives

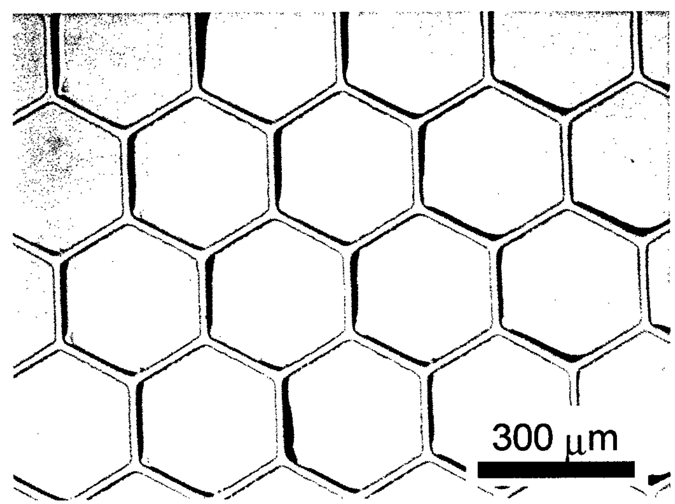
- To fabricate small functional structures of high performance ceramics for potential use in MEMS, microengines

Technical Approach

- Single source ceramic precursors
- Micromolding
- High temperature pyrolysis

Accomplishments

- Si/B/C/N precursors
- Test patterns of such Si/B/C/N ceramic at ~100 μm level



Microelectrochemistry: Saran Wrap Electroplating

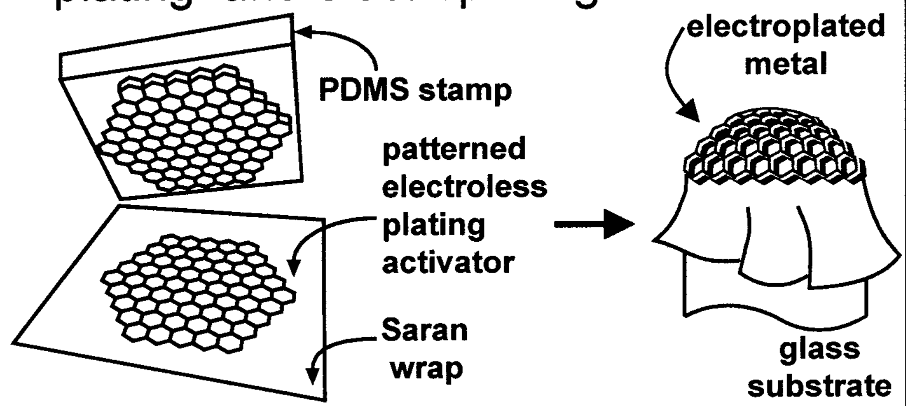
Wilhelm Huck, Scott T. Brittain, Hongkai Wu,
George M. Whitesides, Harvard University

Objective

- To pattern nonplanar, non-cylindrical substrates with feature sizes ranging from 1 to 100 μm.

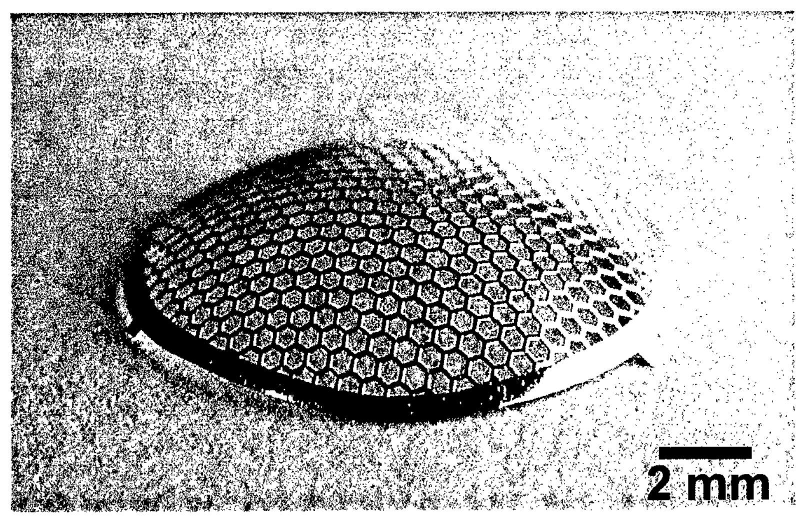
Technical Approach

- μCP, flexible substrates, electroless plating and electroplating



Accomplishments

- Patterned 1 cm radius of curvature over a 60°arc
- Freestanding structures
- ~100 μm feature sizes



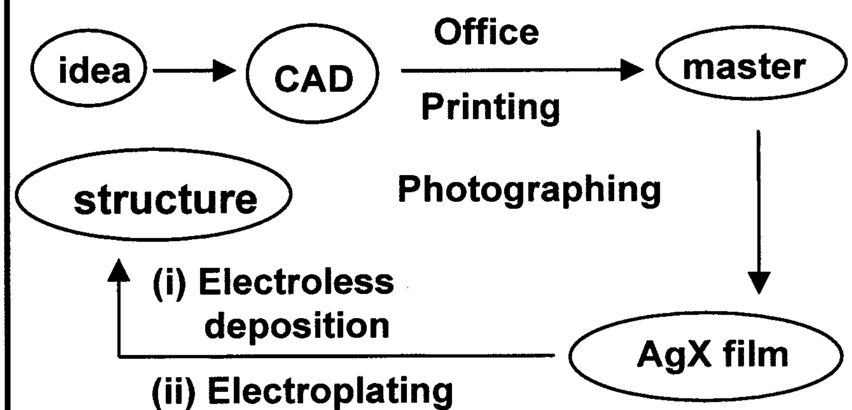
Rapid Prototyping Using Silver Halide-based Film

Tao Deng, F. Arias, R. F. Ismagilov, P. J. A. Kenis,
and George M. Whitesides
Department of Chemistry, Harvard University

Objective

Development of new methods for rapid prototyping of metallic microstructures

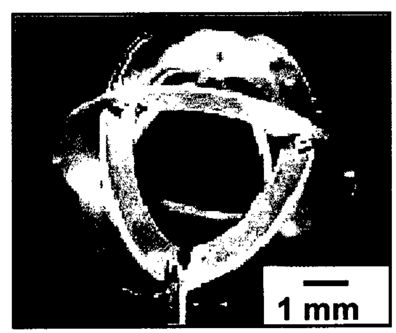
Technical Approaches

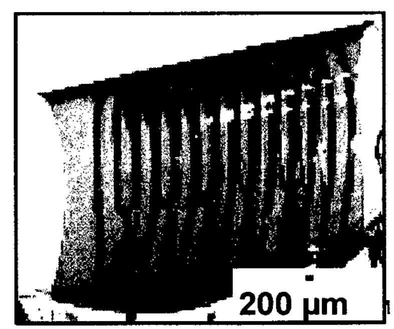


Accomplishments

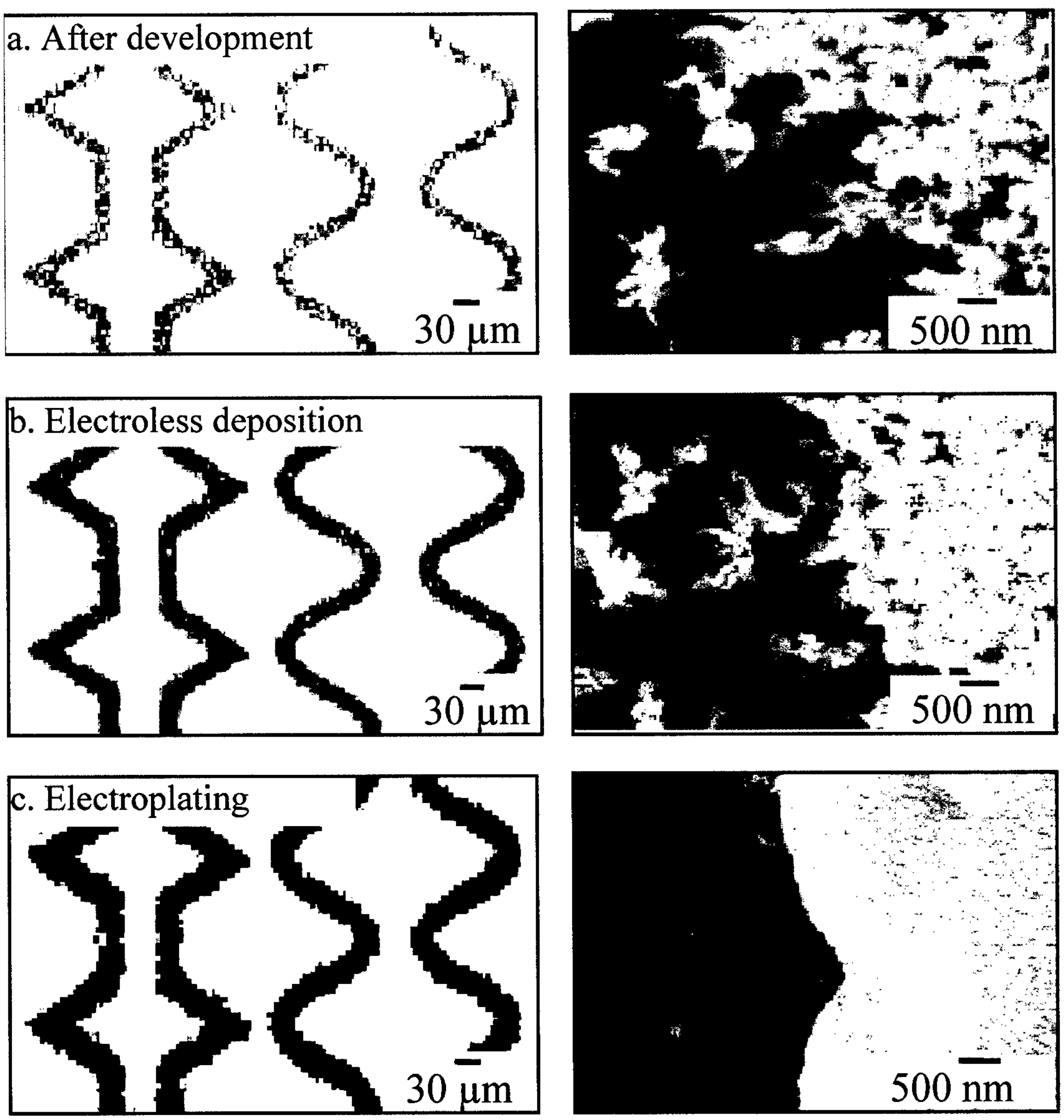
Rapid prototyping metallic structures with >30 μm features:

- Continuous structures
- Discontinuous structures
- 3D structures
- HAR structures





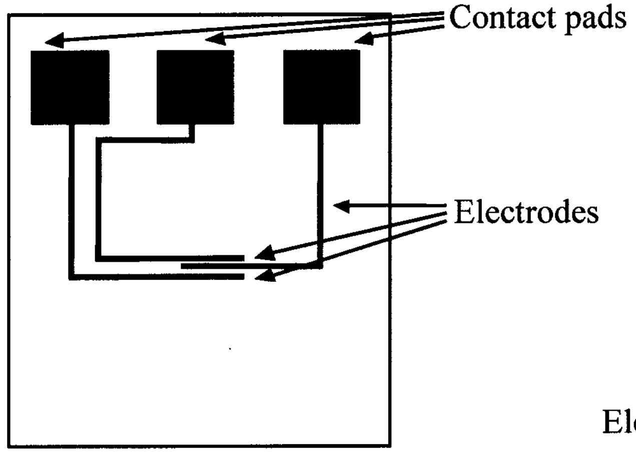
Gold Lines Fabricated using Silver Halide-based film



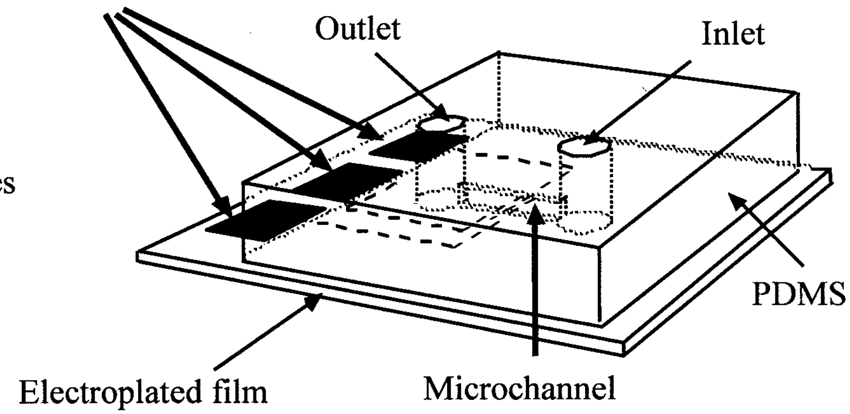
T. Deng, F. Arias, P. Kenis, R. Ismagilov, and G. M. Whitesides

Electrochemical Detector for Microfluidic Systems

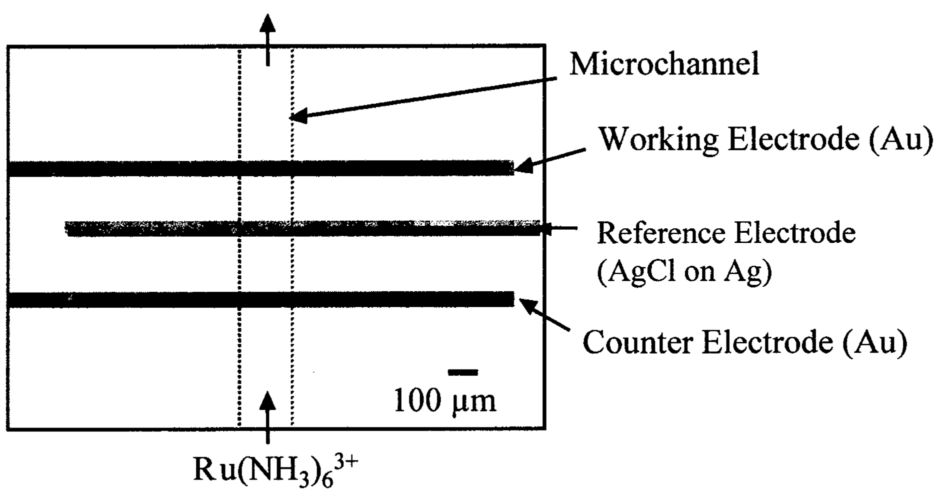
1. Design



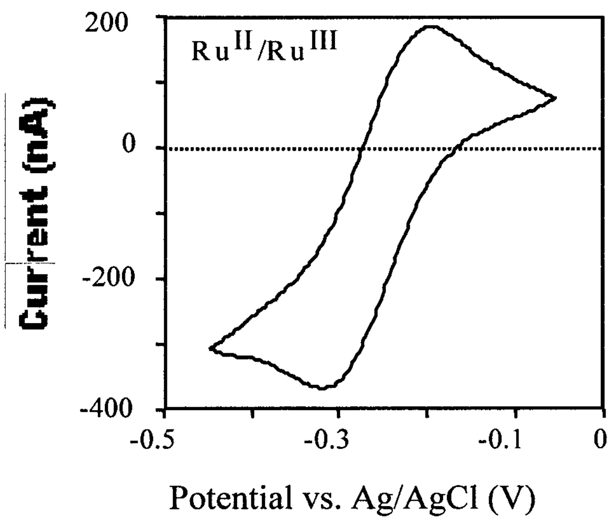
2. Three Electrode System



3. Magnified view



4. Cyclic Voltammetry



T. Deng, F. Arias, P. Kenis, R. Ismagilov, and G. M. Whitesides

Fabrication of 3D Microfluidic Systems

Anderson, Chiu, Jackman, Cherniavskaya, McDonald, Wu, Whitesides, and Whitesides
Department of Chemistry and Chemical Biology, Harvard University

Objectives

- To fabricate membranes of PDMS with ~50-100 μm microfluidic channels of any topology
- To align, stack, and seal these membranes to make a more complicated 3D geometries

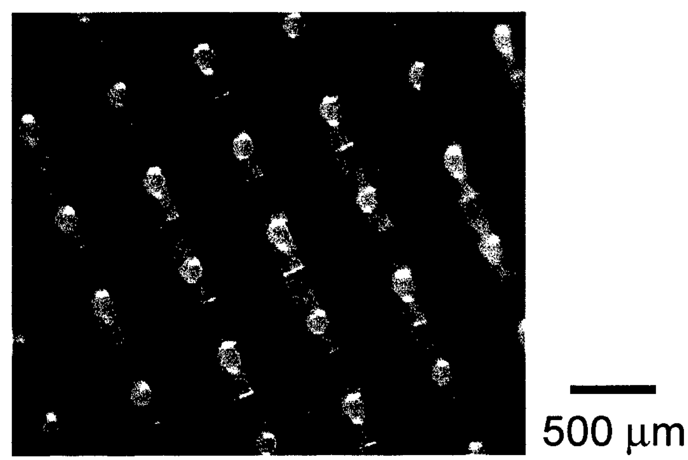
Technical Approach

- Rapid Prototyping
  - Multi-level Photolithography
- Membrane Sandwich Method
  - Supported Membrane Transfer

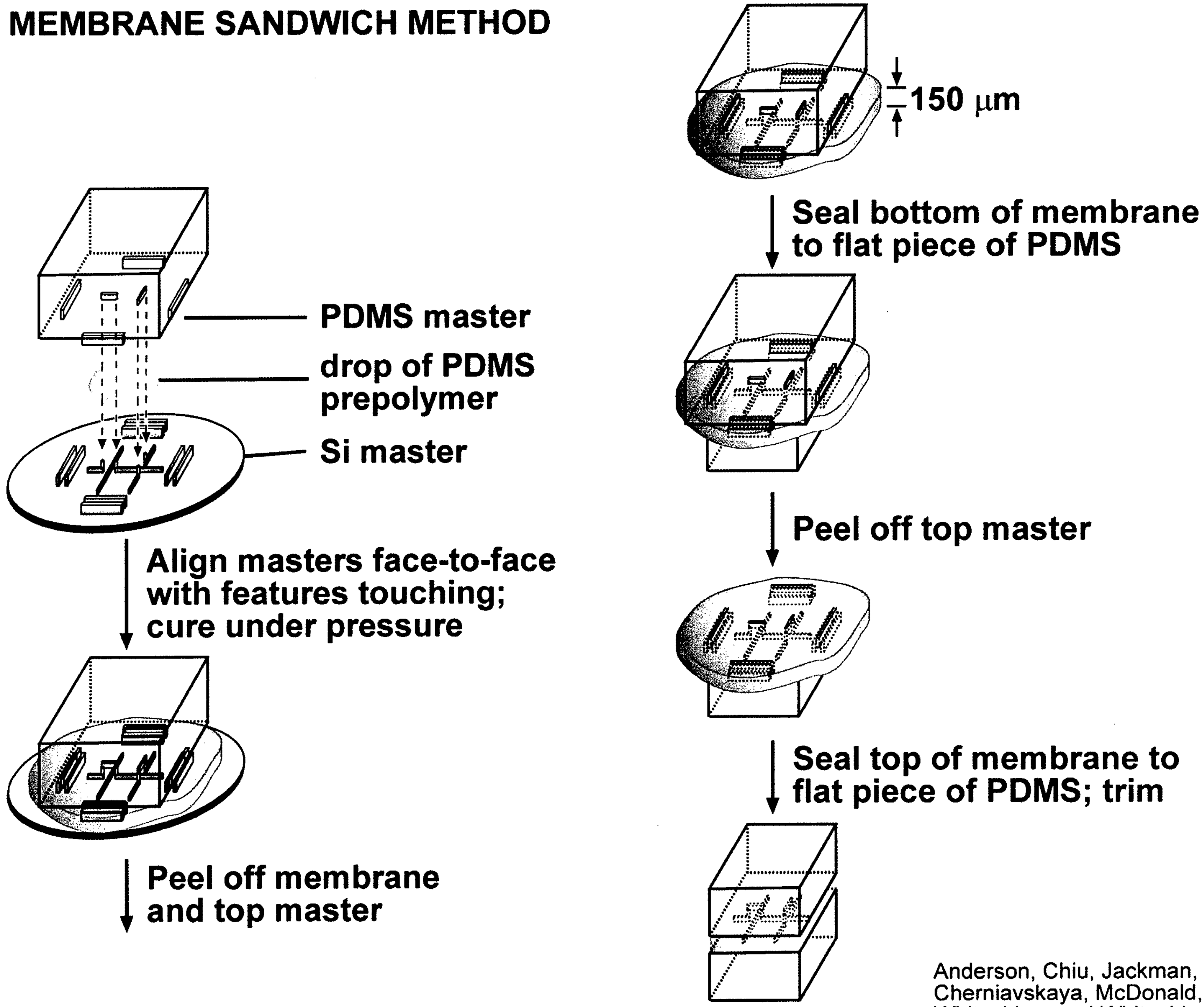
Accomplishments

- We make channels in a single membrane that cross over and under each other without intersecting
- We can make *any* microfluidic knot
- We can transfer discontinuous features between substrates without distortion

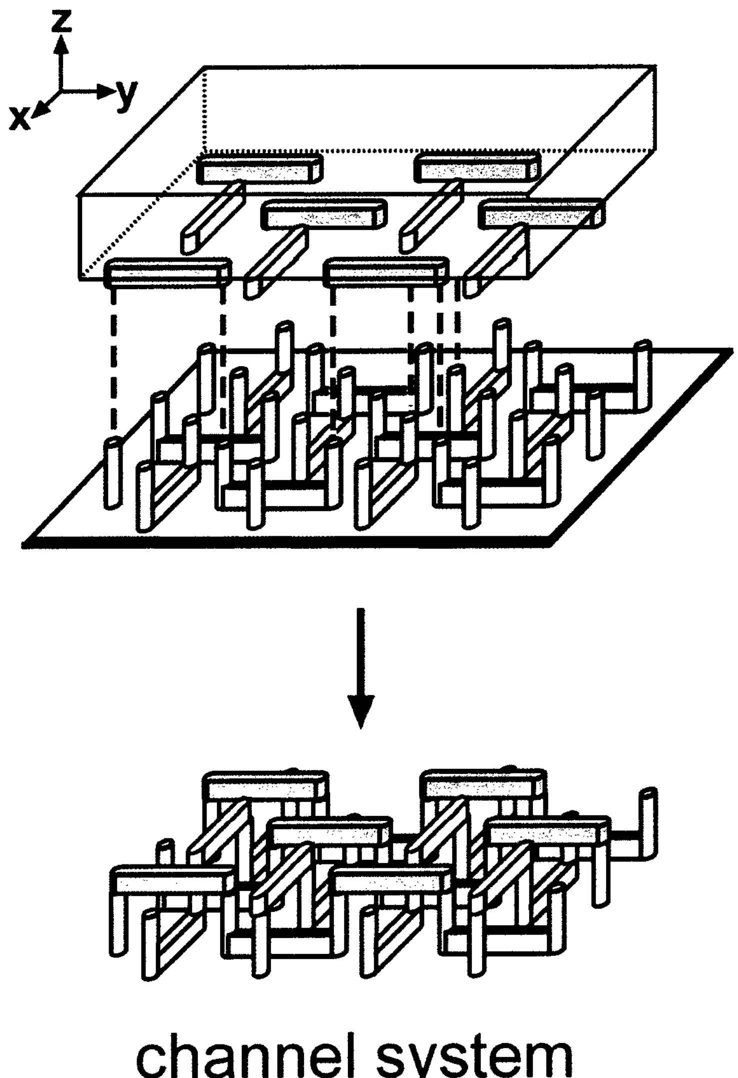
"Basket weave" system

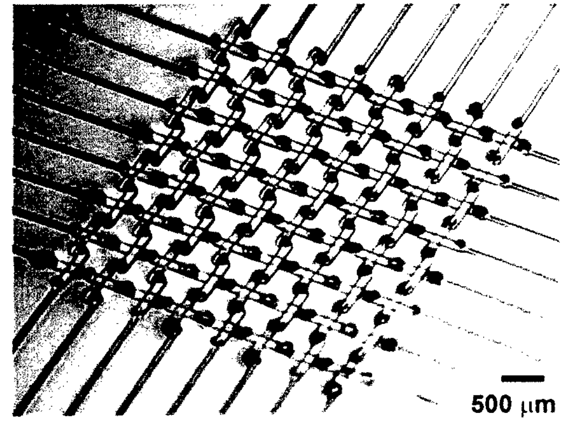


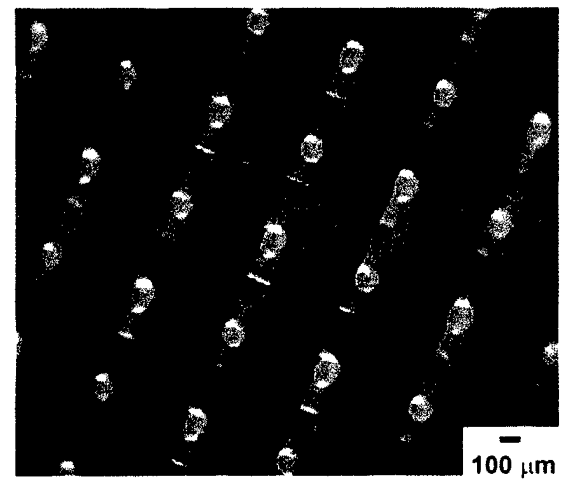
MEMBRANE SANDWICH METHOD

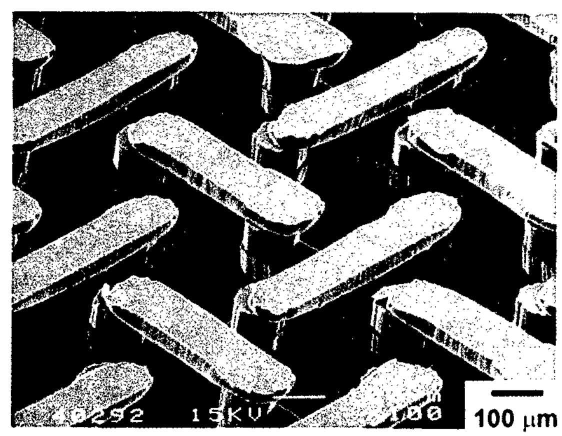


Anderson, Chiu, Jackman, Cherniavskaya, McDonald, Wu, Whitesides, and Whitesides

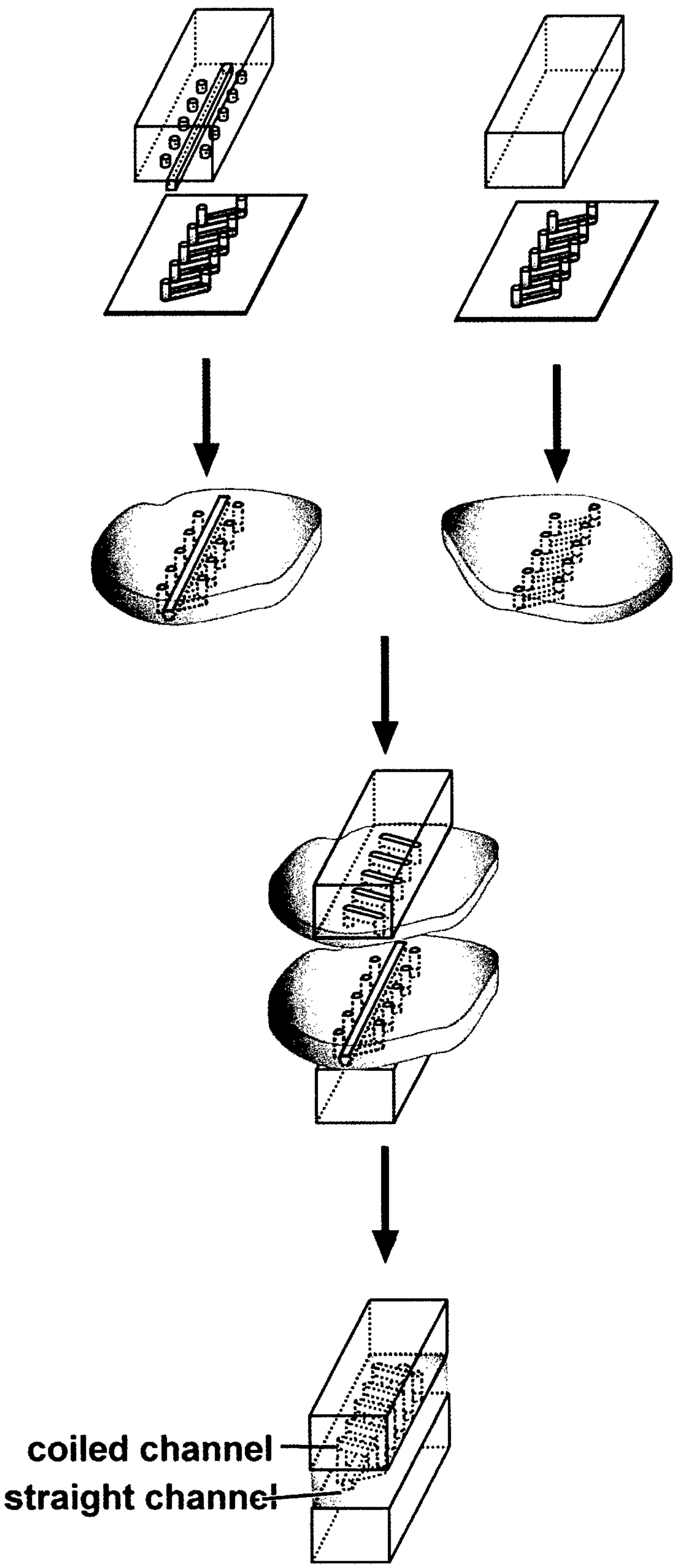


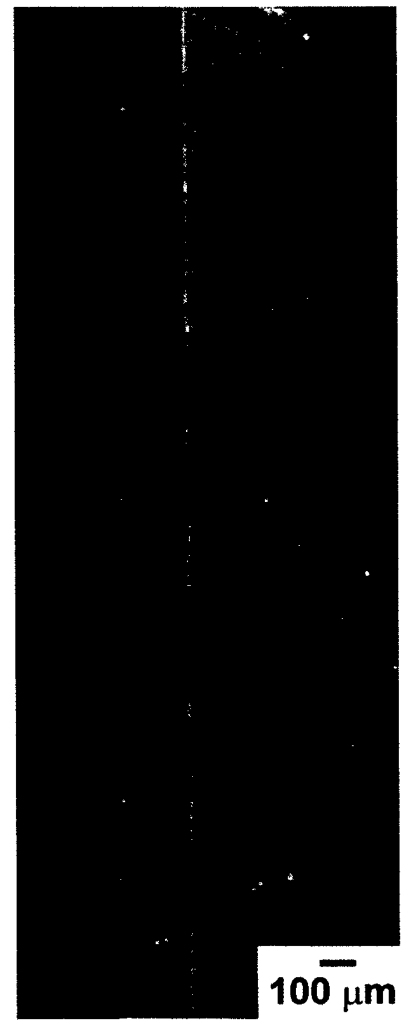






Anderson, Chiu, Jackman, Cherniavskaya, McDonald, Wu, Whitersides, and Whitesides





Anderson, Chiu, Jackman, Cherniavskaya, McDonald, Wu, Whitersides, and Whitesides

Three-Dimensional Self-Assembly of Micron-Sized Objects

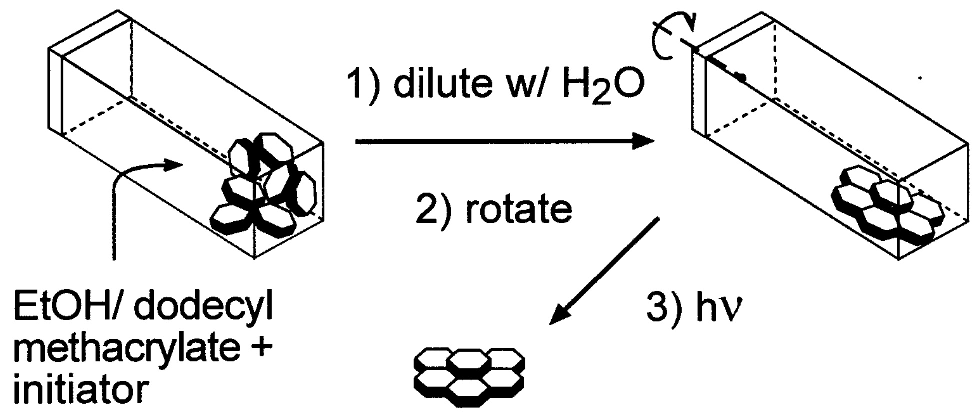
Joe Tien, Thomas D. Clark, and George M. Whitesides

Department of Chemistry, Harvard University

Objective:

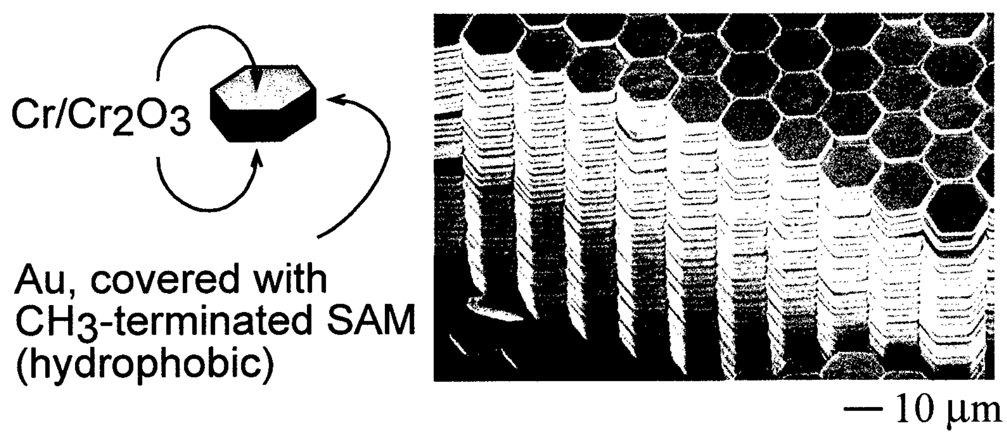
To develop methods for 3-dimensional microfabrication based on self-assembly

Approach: Crystallization Using Capillarity



Accomplishments:

- Facile construction of ordered, 3-dimensional microarrays from non-spherical subunits.
- Bridges gap between colloidal and millimeter-scale self-assembly.
- Likely extendable to other polyhedral components.



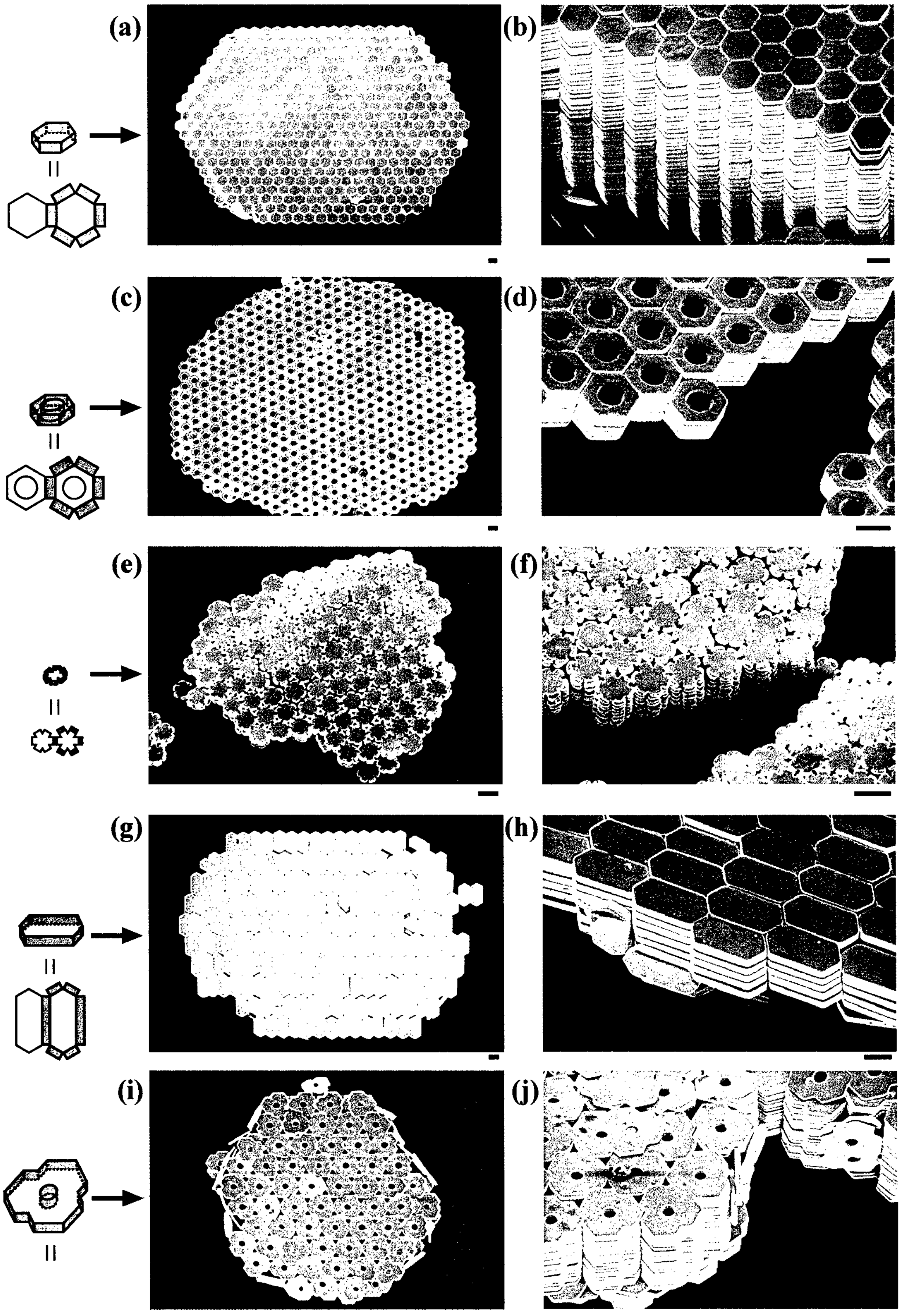


Figure 2

Fabrication of Dali's Crosses

Hong Yang, Francisco Arias, and George M. Whitesides
Department of Chemistry & Chemical Biology, Harvard University

Objectives

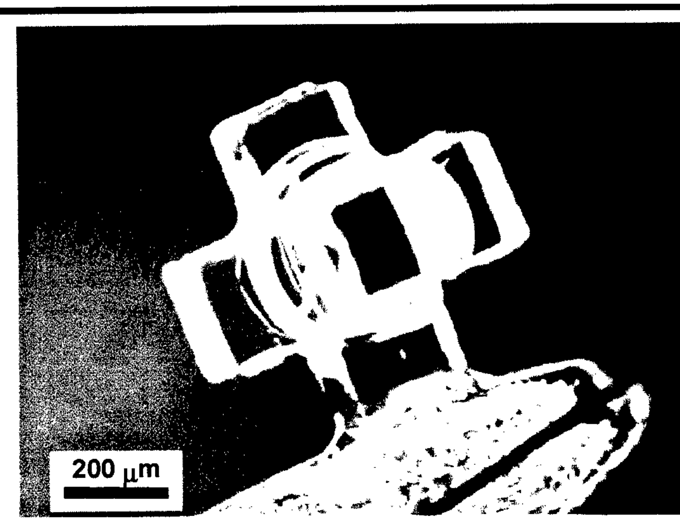
- To demonstrate 3D fabrication and use the crosses as building units for self-assembled structures

Technical Approach

- UV-curable prepolymers
- Multilayer registration
- Micromolding

Accomplishments

- Fabricated polymeric Dali's crosses
- Three-level registration to ~ 100 μm



Future Directions: Near Term

Microorigami, composites and trusses (μUAVs, read arms)

- tensegrity structures—incorporation of polymeric elements into metallic, 3D structures
- maximize the stiffness-to-weight ratio of the panels
- use diffusion bonding of nickel instead of tin/lead soldering to assemble sandwich panels

Slot filters (thermophotovoltaics)

- smaller critical dimensions (~100 nm line width)
- fabrication on curved surfaces

Heat exchangers (high power microelectronics)

- modules with high surface area and low thermal resistance
- non-planar heat exchangers

Microcontact printing on curved/spherical surfaces
(curved focal plane IR detector)

- solve the distortion problem for printing on spherical surfaces
- additive methods
- functional components

FLO for fabrication of microelectrode systems (BWD)

- integrated micro-analysis systems
- use for logic/problem solving

Dali crosses (photonic bandgap materials)

- increase yield and quality of the crosses
- modify faces of the crosses and self-assemble into ordered 3D structures

Future Directions: Far Term or Technology Base

Rapid prototyping using Soft Lithography

- generate structures at 1-μm scale

Microelectrochemistry on Saran Wrap (curved surface fabrication)

- quantify and minimize distortion during stretching
- reduce feature size to 1 μm

Self-assembly (3D electronic circuits)

- controlling assembly size and shape through templating
- add transistors to the faces
- Self-assembly of photonic bandgap crystals

Rapid prototyping using silver halide film

- smaller structures; more functional applications, color films

Ceramics (rapid microfabrication of complex ceramic microstructures)

- C/Si: new start to convert Si layer on glassy C to SiC
- Si/B/C/N: improve fidelity; fabricate useful structures such as membranes and microcomponents

3D microfabrication in microfluidic systems (BWD)

- apply methods to systems that require compactness or have topological constraints
- generate complex fluidic components

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

Micropatterning through Field-Assisted Flow

ILHAN A. AKSAY[*,§], GEORGE M. WHITESIDES[†], SOL M. GRUNER[‡], ROBERT K. PRUD'HOMME[*,§], DUDLEY A. SAVILLE[*,§], JAMES S. VARTULI[*,§], DANIEL M. DABBS[*,§], MATT TRAU[§], SRINIVAS MANNE[§], LINBO ZHOU[#], ANTHONY KU[*,§], HAK FEI POON[*,§], MACIT ÖZENBAS[§]

DEPARTMENTS OF [*]CHEMICAL ENGINEERING, [#]PHYSICS, AND [§]PRINCETON MATERIALS INSTITUTE
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08544

[†]DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS 02138

[‡]DEPARTMENT OF PHYSICS, CORNELL UNIVERSITY
ITHACA, NEW YORK 14853

FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

Department of Chemical Engineering and
Princeton Materials Institute
Princeton University

Patterning through Field-Assisted Flow

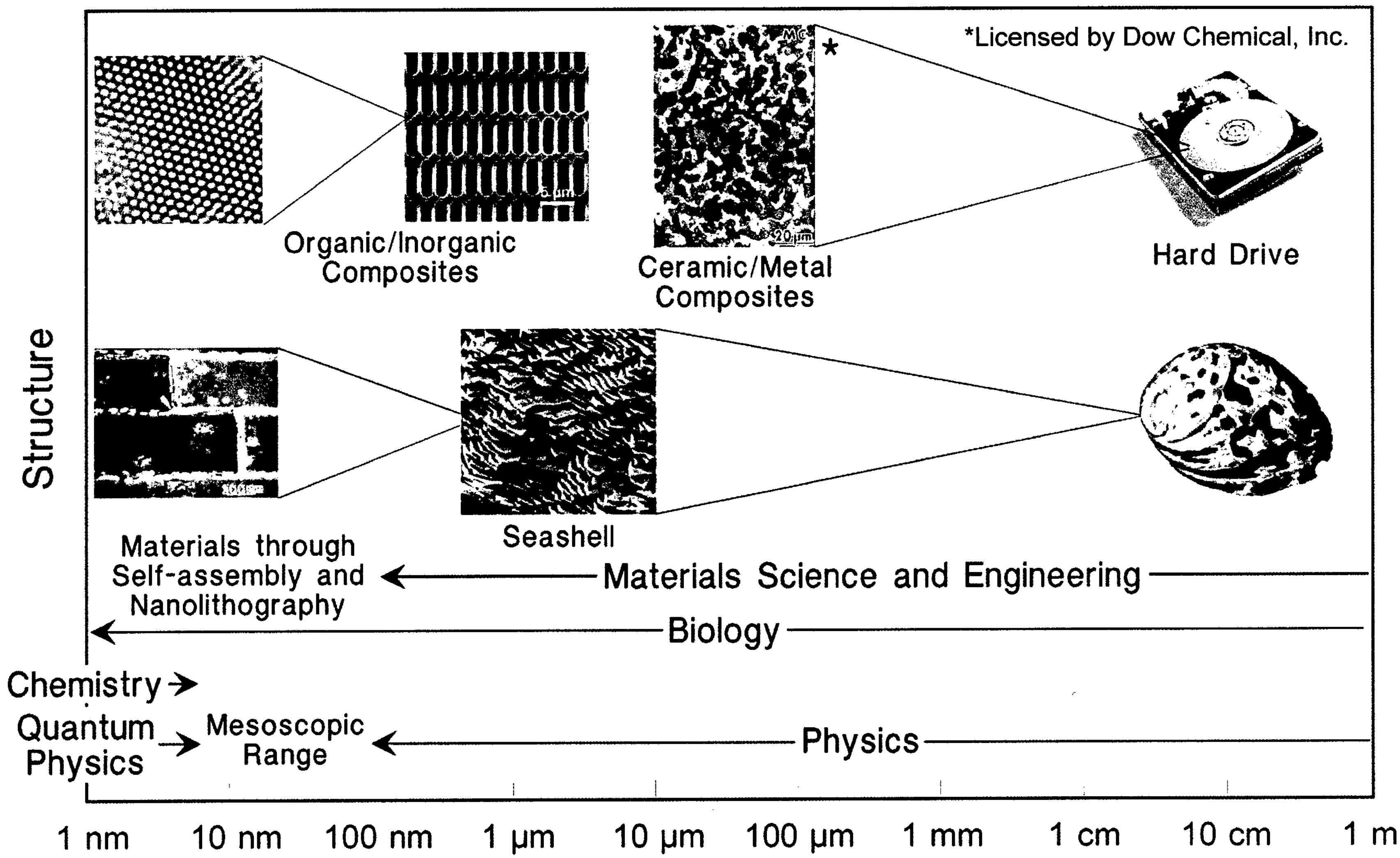
Ilhan A. Aksay,[§] George M. Whitesides,[#] Dudley A. Saville,[§]

Daniel M. Dabbs,[§] Matt Trau,[§] Linbo Zhou,[‡] Anthony Ku,[§]
Hak-Fei Poon,[§] and Macit Özenbas[§]

Departments of [§]Chemical Engineering, [‡]Physics,
and Princeton Materials Institute,
Princeton University

[#]Department of Chemistry, Harvard University

Scale of Materials Processing

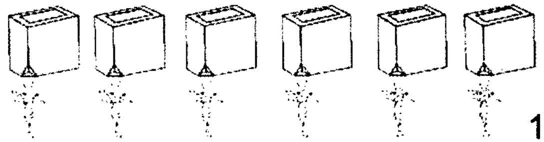


Goals and Organization

PROCESSING TECHNIQUES

Self Assembly

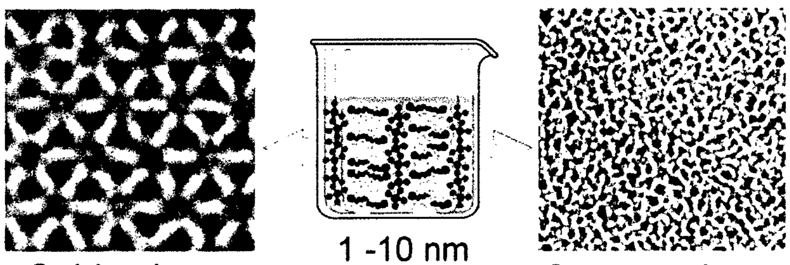
(a) Amphiphilic and Protein Membranes



1 -10 nm

Groves, Hecht, Aksay (NSF)

(b) Liquid Crystal Templating



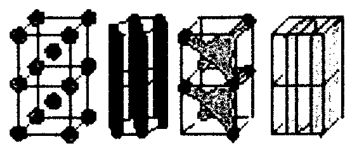
Cubic phase

1 -10 nm

Sponge phase

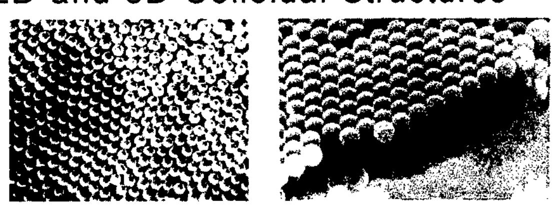
Dabbs, Saville, Aksay

(c) Block Copolymer Templating (NSF)



10 - 100 nm

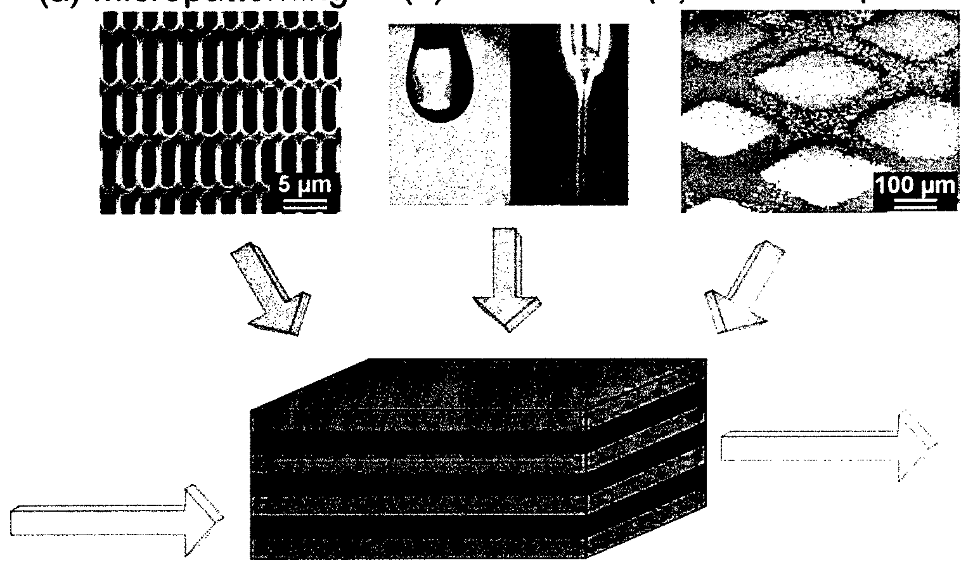
(d) 2D and 3D Colloidal Structures



Saville, Aksay

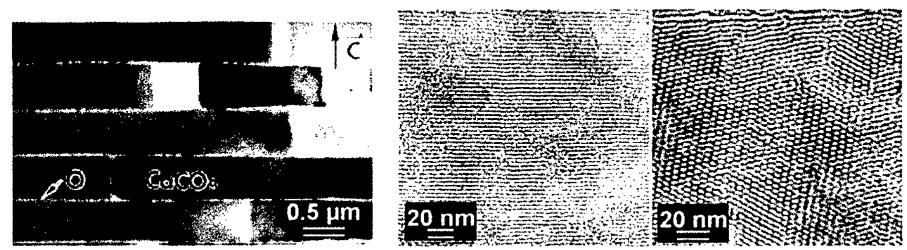
Laminating and Micropatterning by Field-Assisted Flow

(a) Micropatterning (b) Cone/Jet (c) Electrodeposition



Hierarchically Structured Nano- and Microlaminates

Suo, Evans, Soboyejo, Saville, Groves, Aksay (NSF)



OPTIMAL PROPERTIES

Patterned Thin Films and 3D Structures

- ***Goals***
  - **Develop nanostructured ceramic/organic composites through self-assembly**
  - **Develop patterned structures for device applications**
- ***Conventional Approach***
  - **Deposit continuous ceramic films followed by etching**
    - Photolithographic resolution is large (>0.1 μm)
    - Expensive and hazardous etchants

Department of Chemical Engineering and
Princeton Materials Institute
Princeton University

Confinement Patterning: Simultaneous Patterning at Multi-Length Scales

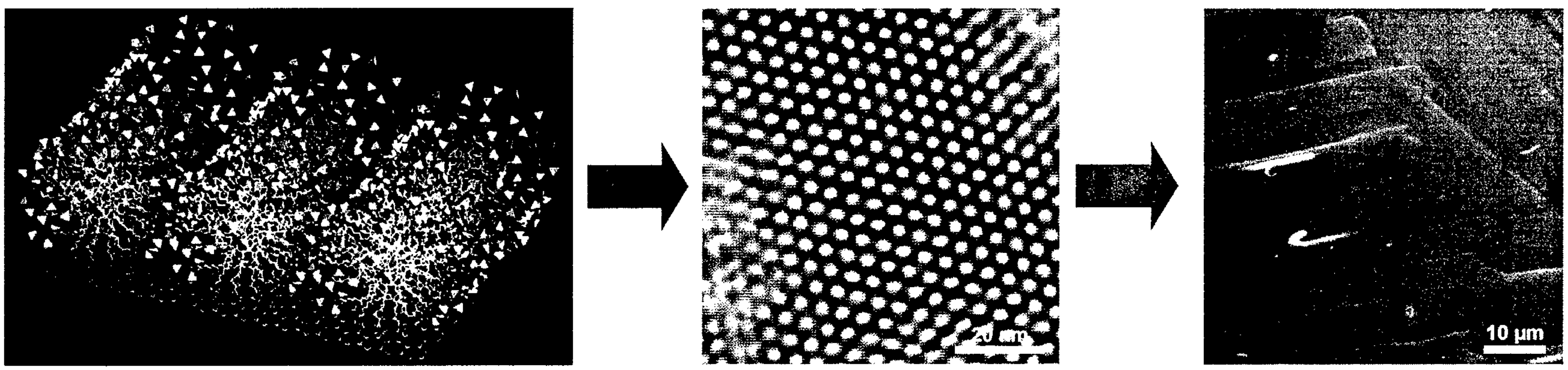
Anthony Y. Ku, Linbo Zhou,
Dudley A. Saville,* Peter Eisenberger,*
George M. Whitesides, and Ilhan A. Aksay

*Partial support from the NSF/MRSEC (DMR 94-00362 and DMR 98-09483)

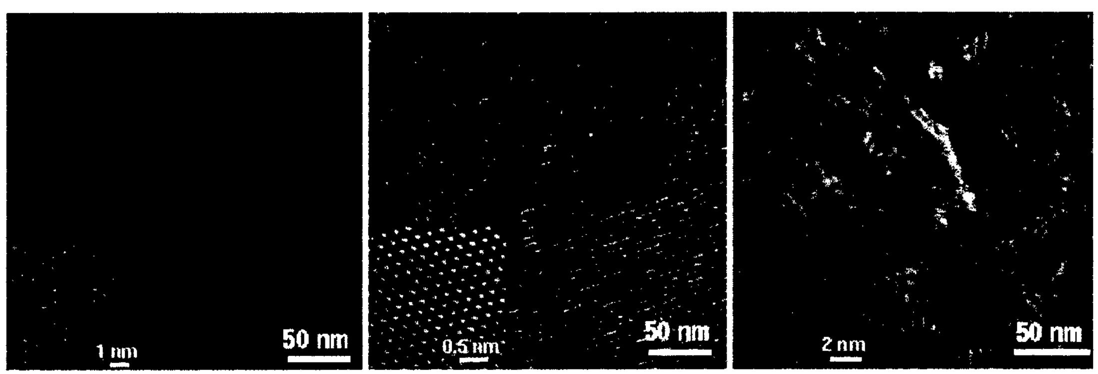
Mesostructured Inorganics through Liquid Crystal Templating

• ***Surfactant-based procedure yields mesostructured inorganic materials***

C. T. Kresge *et al.*, *Nature* **359** (1992); and, J. S. Beck *et al.*, *J. Am. Chem. Soc.* **114** [27] (1992).



I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, S. M. Gruner *Science* **273** 892–98 (1996).



Mica Graphite Silica

Projected and Actual Applications

Biocomposites
- artificial coral[1]
- bioreactor frameworks

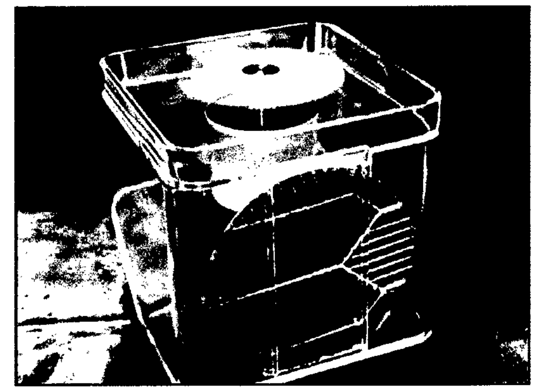
Catalysis[2]

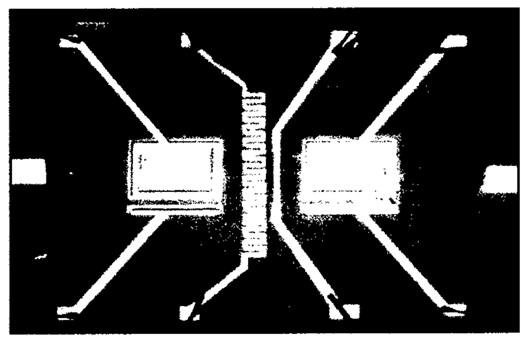
Low dielectric films[3]

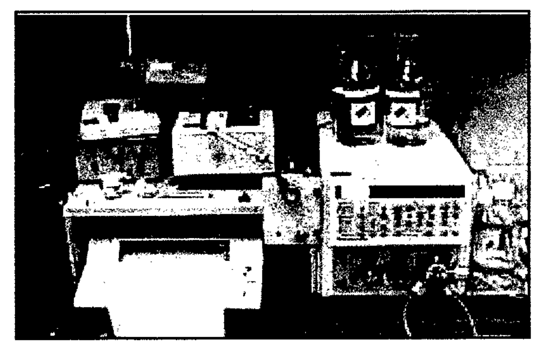
Nanoelectronics
- lasers[1]
- memory components

Sensors

Separations
- biological
- environmental[1,3-4]
- HPLC column packing[4]
- others (embedded films[3])

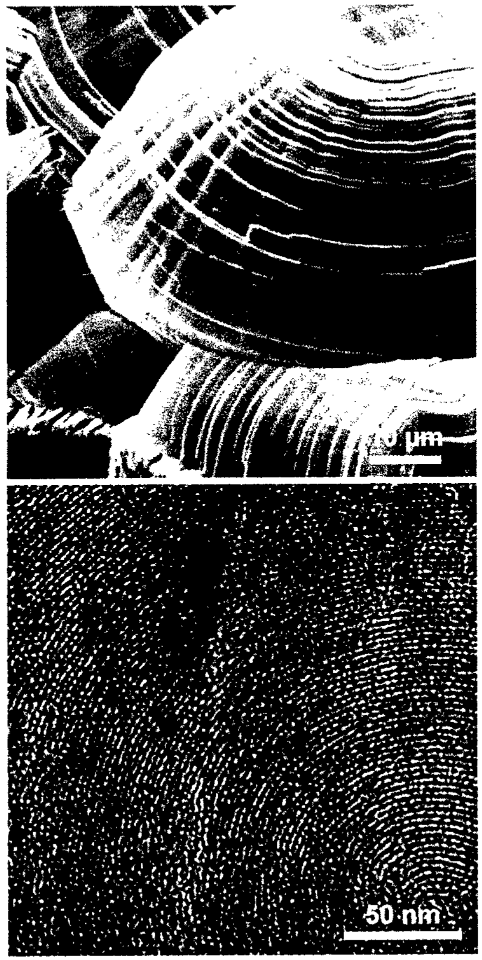






[1] UC-Santa-Barbara
[2] Mobil Oil Company
[3] Pacific Northwest National Lab
[4] Los Alamos National Lab

Nanocomposite Organic/Inorganic Materials through Self-assembly



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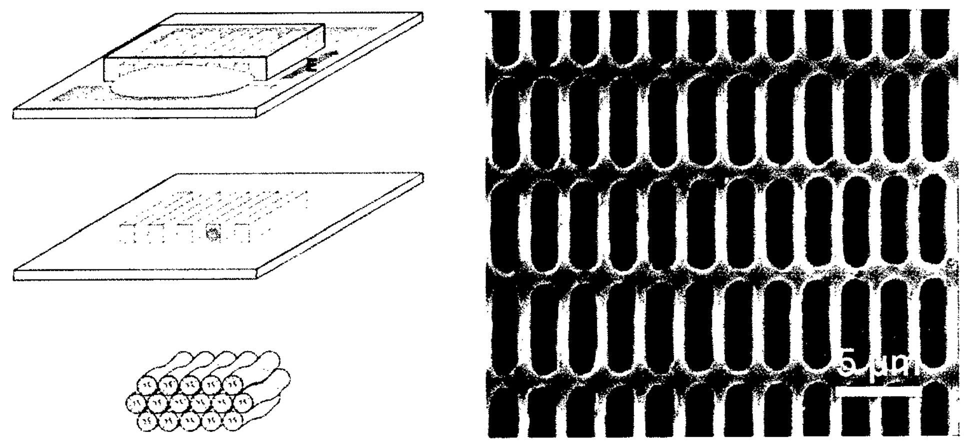
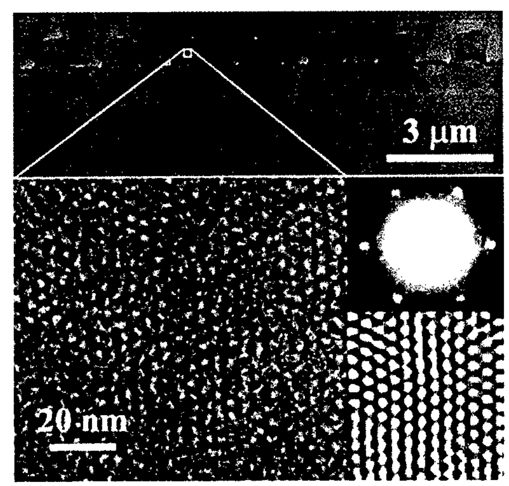
Micropatterning

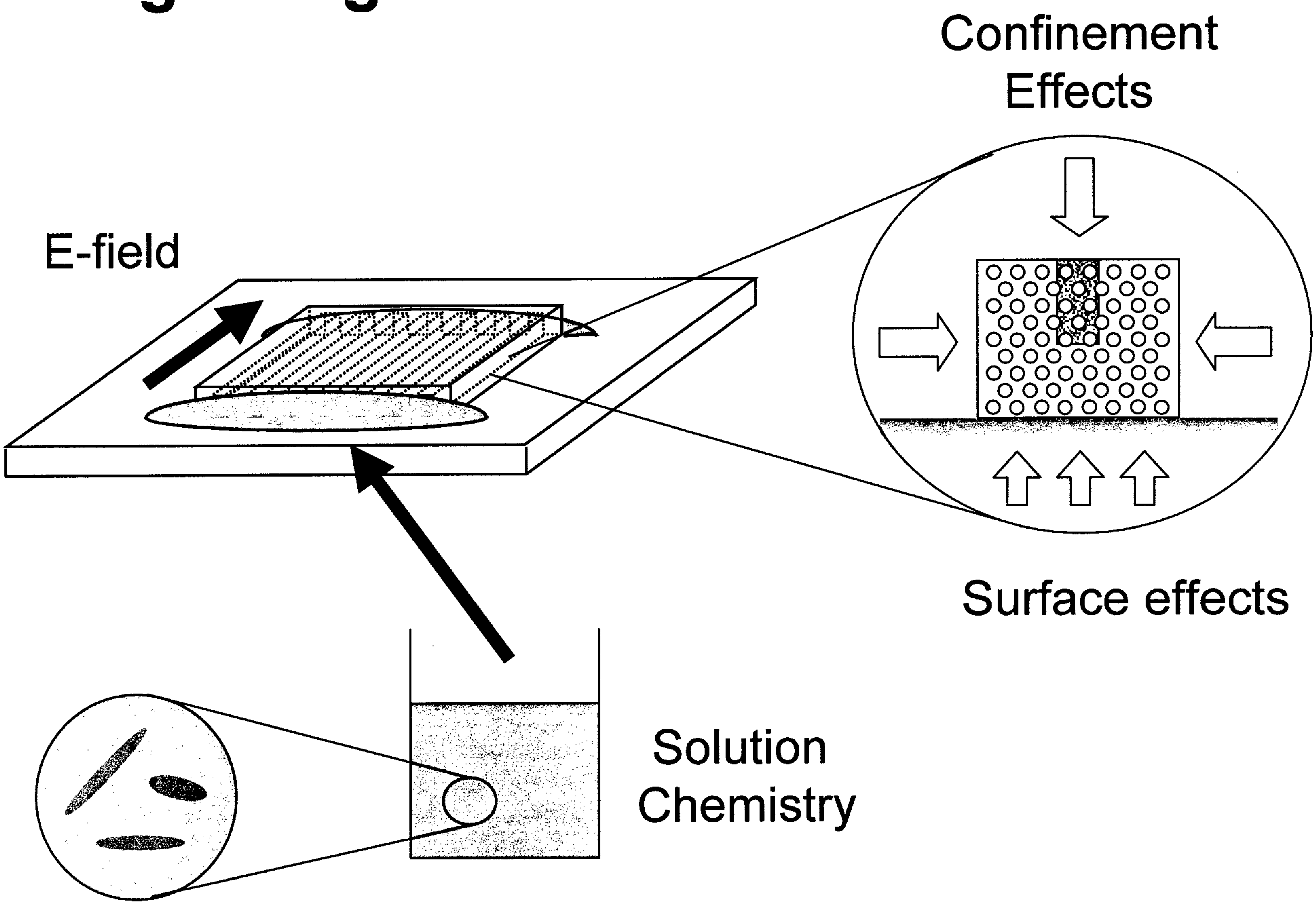


Hexagonal Phase

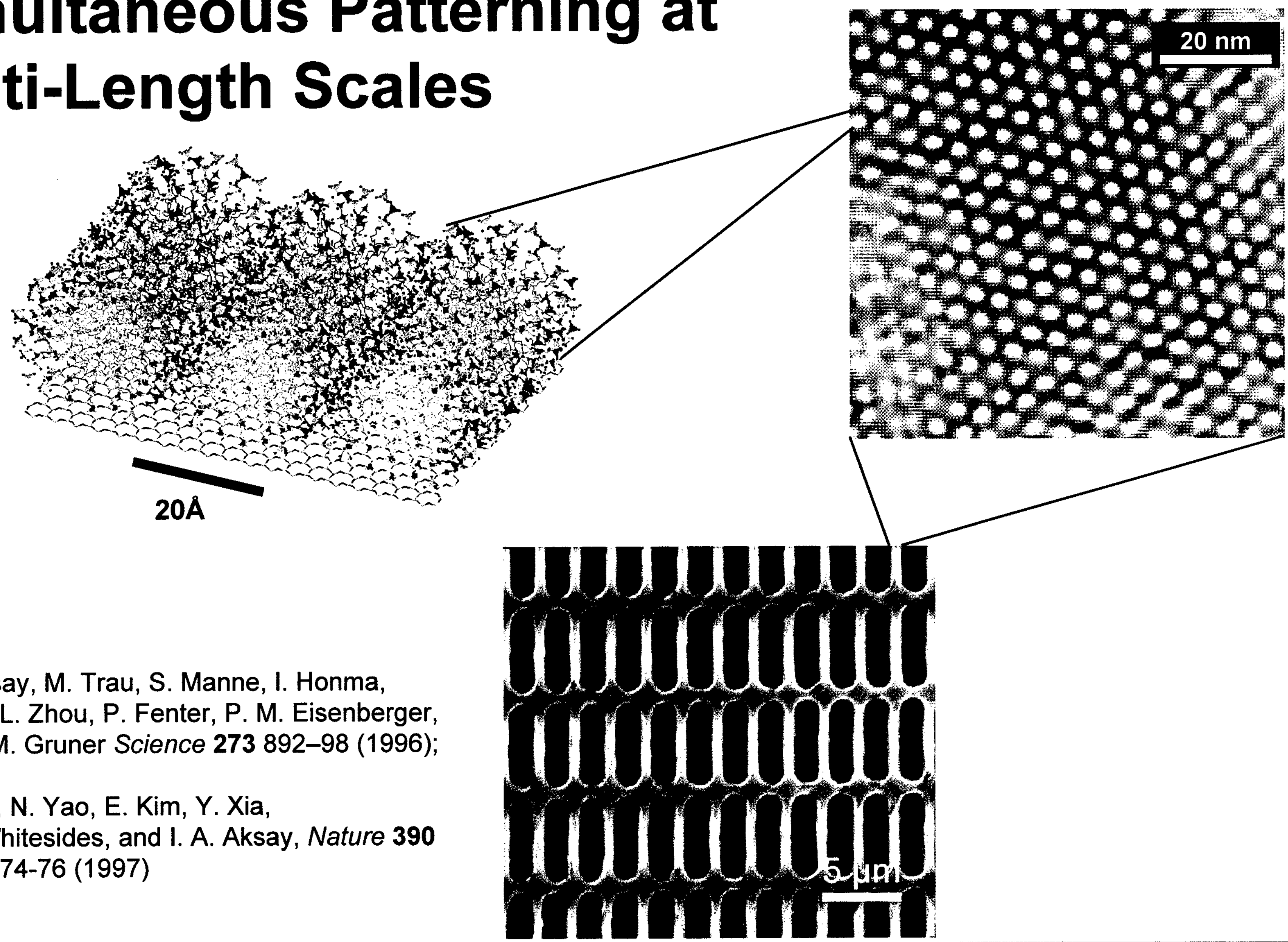


M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides, I. A. Aksay, *Nature* **390** 674-6 (1997).

Putting It Together...



Simultaneous Patterning at Multi-Length Scales



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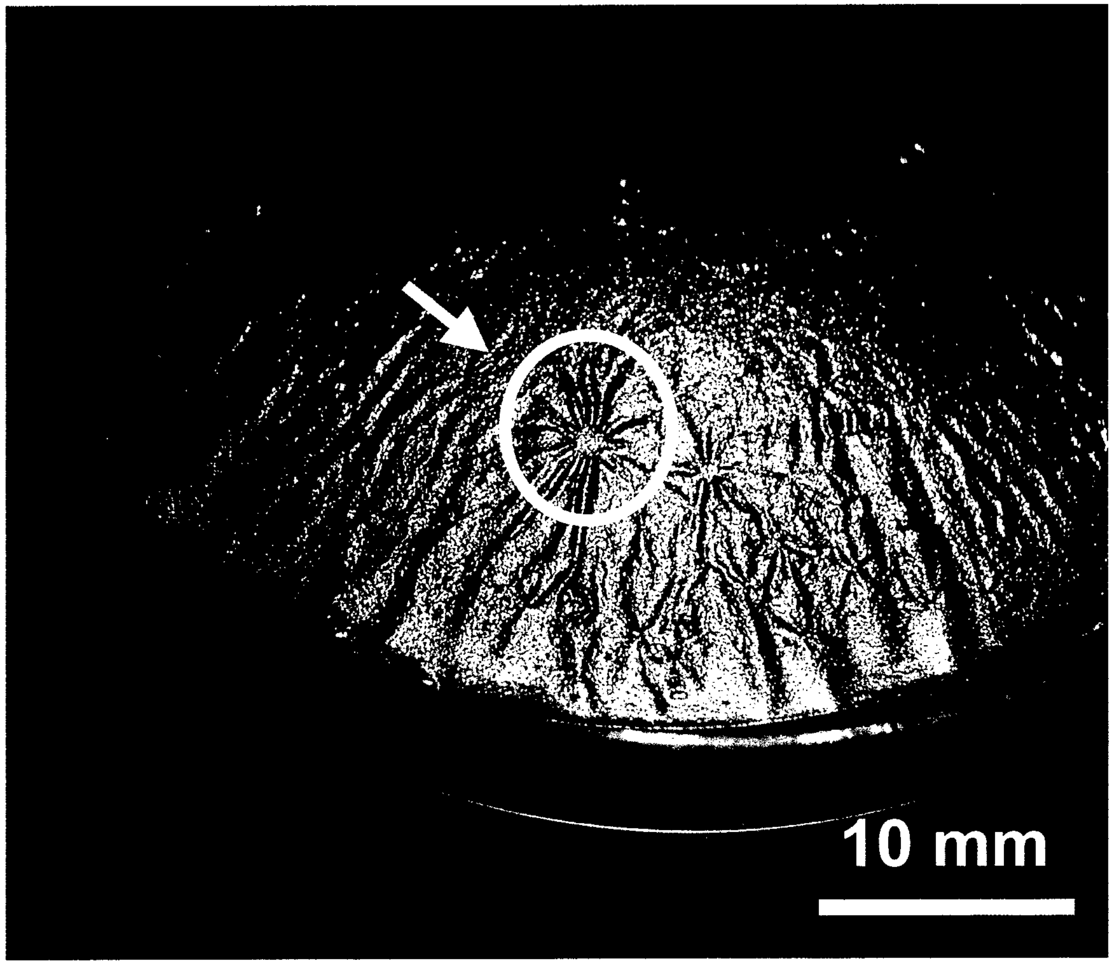
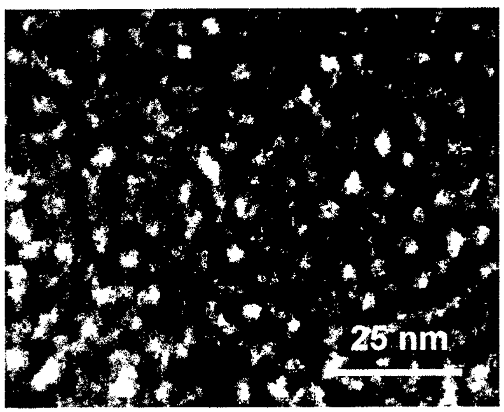
M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides, and I. A. Aksay, *Nature* **390** [6661] 674-76 (1997)

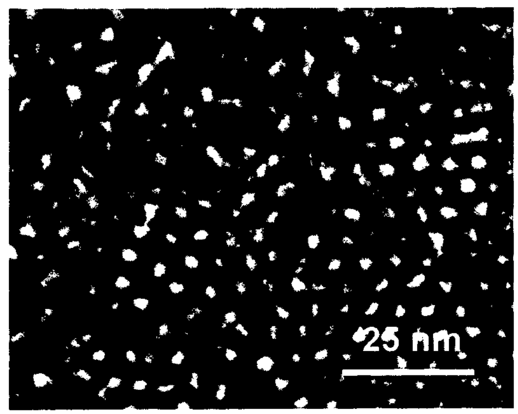


N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)

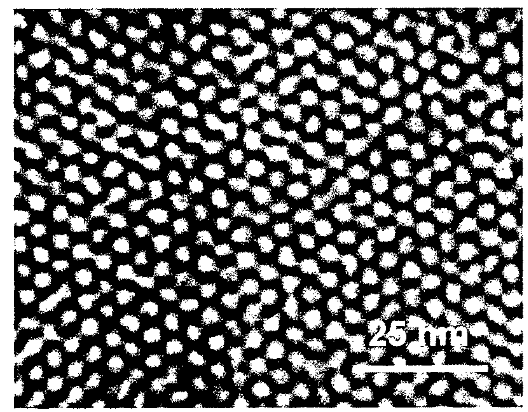
Film Growth: Mesoscopic Crystallization



30 minutes

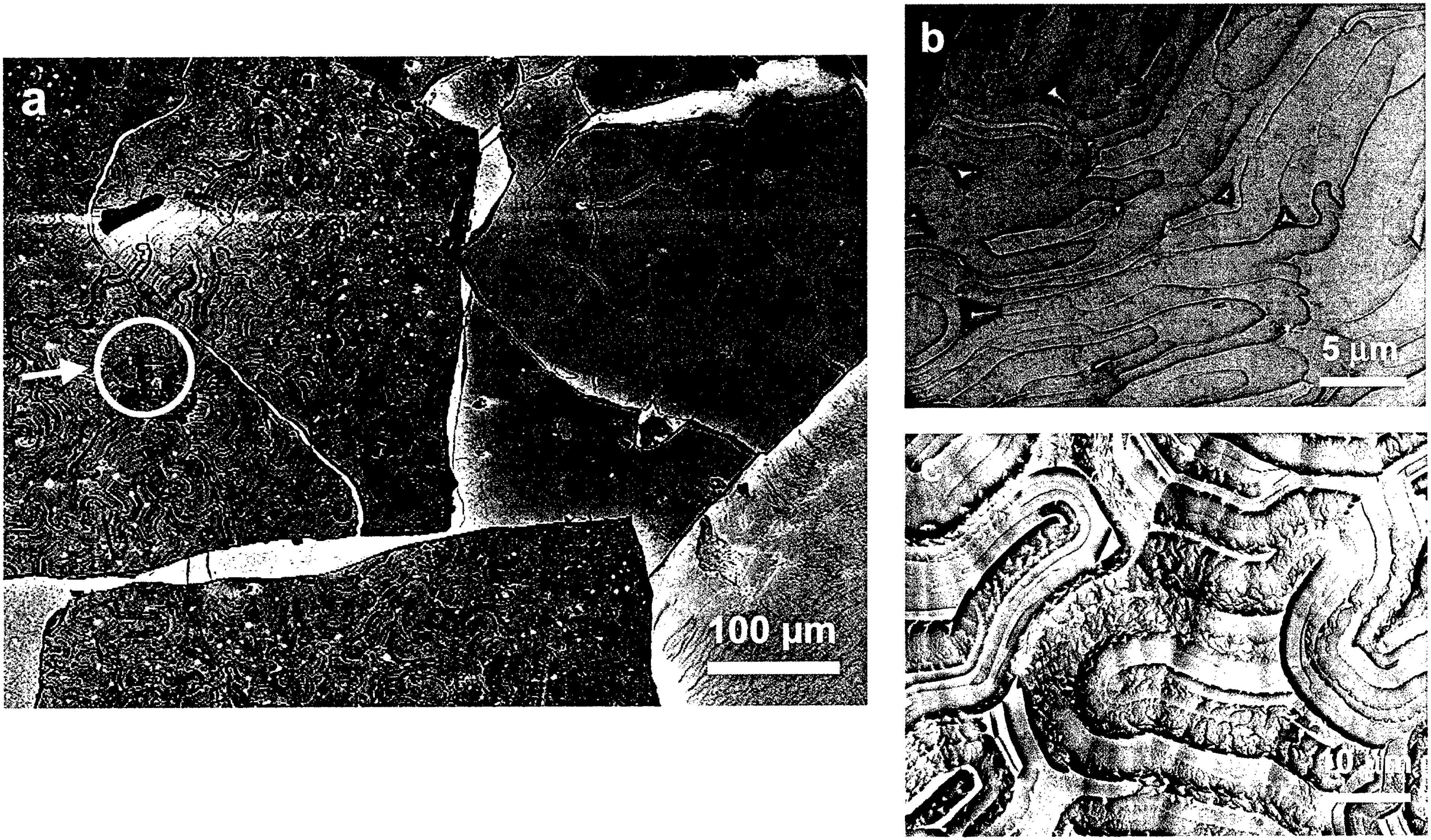


5 hours



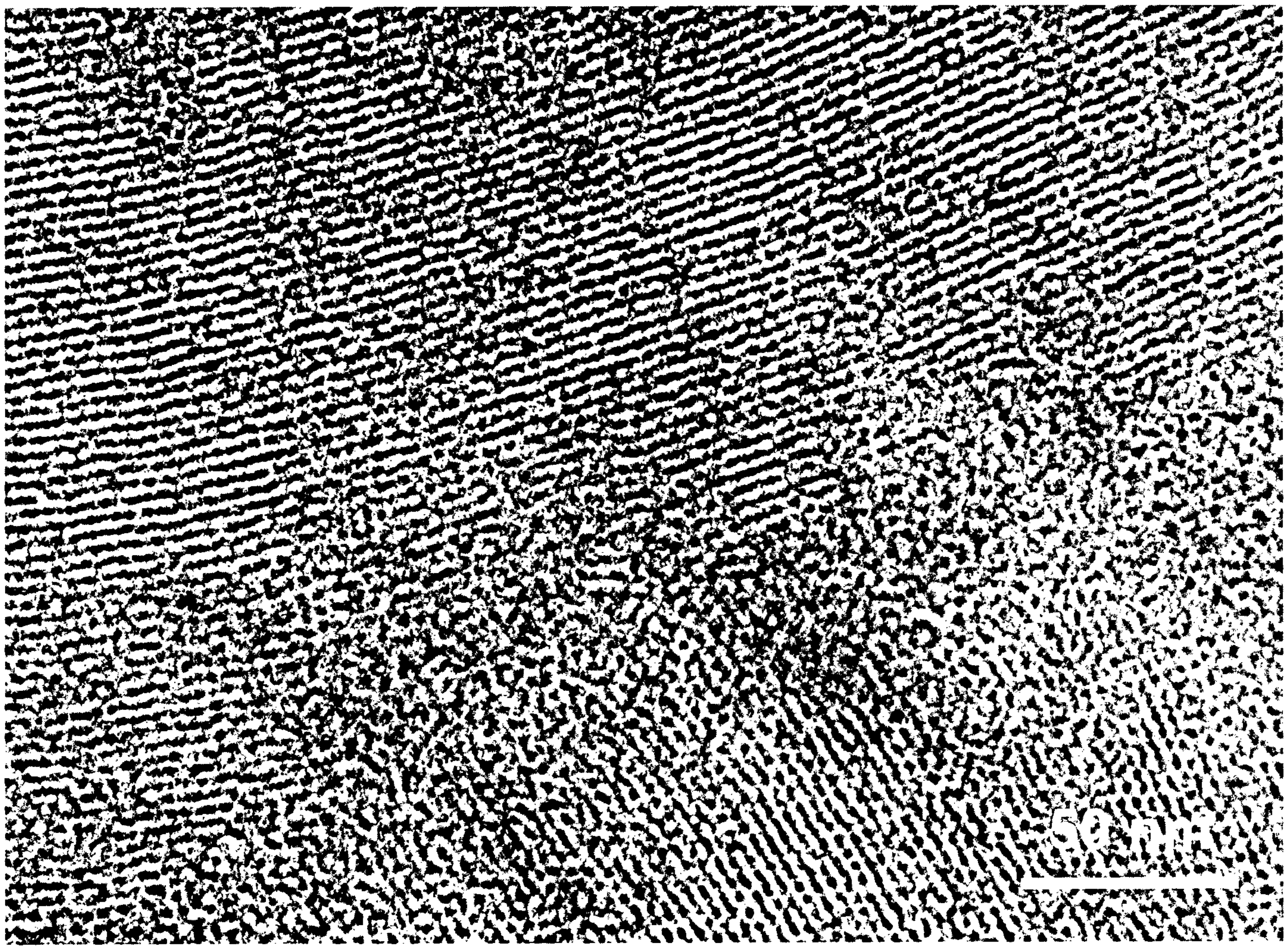
2 days

N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)



N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)

Cross-Sectional TEM:
Film at the Air-Water Interface



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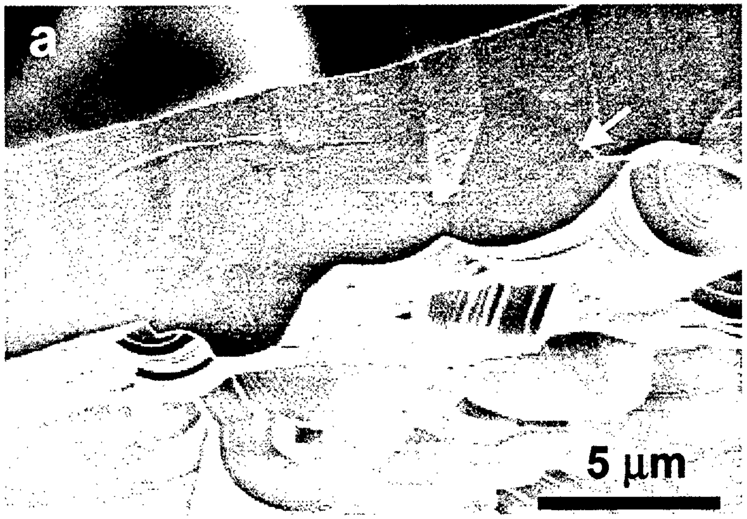
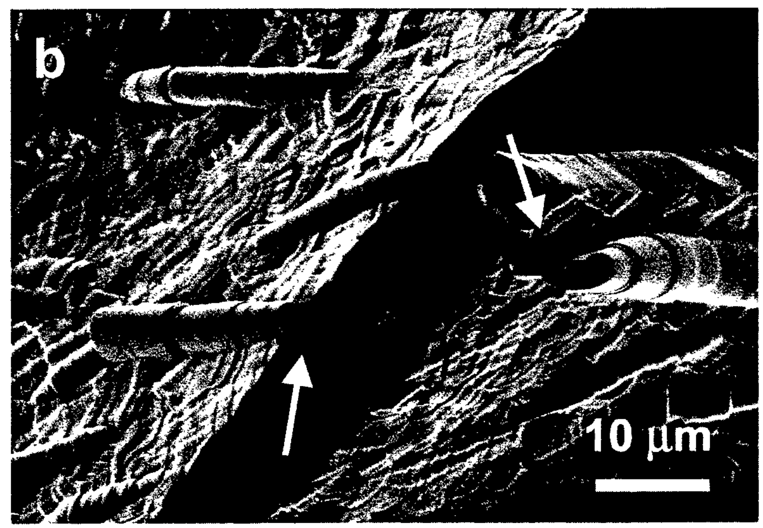
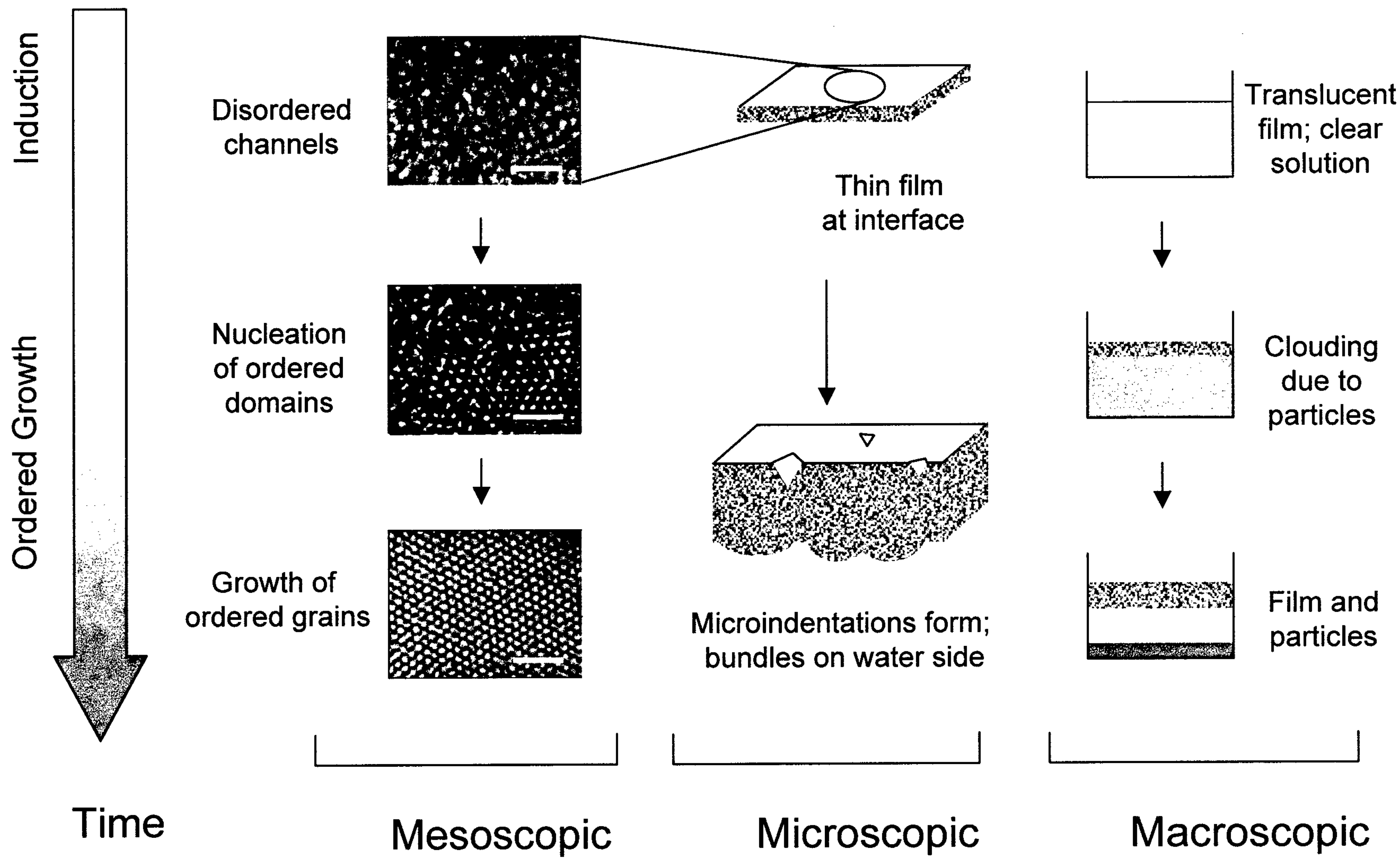




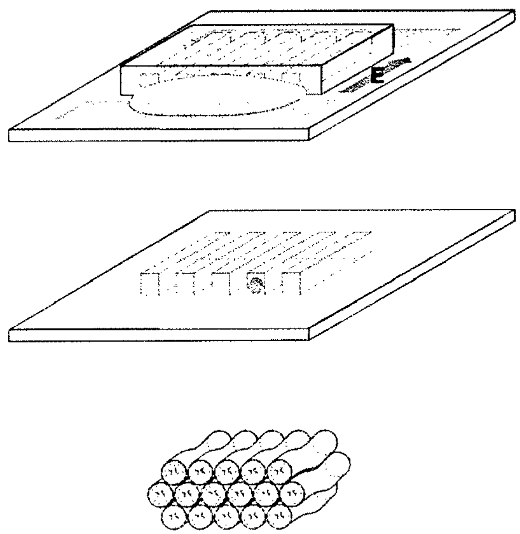
N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)

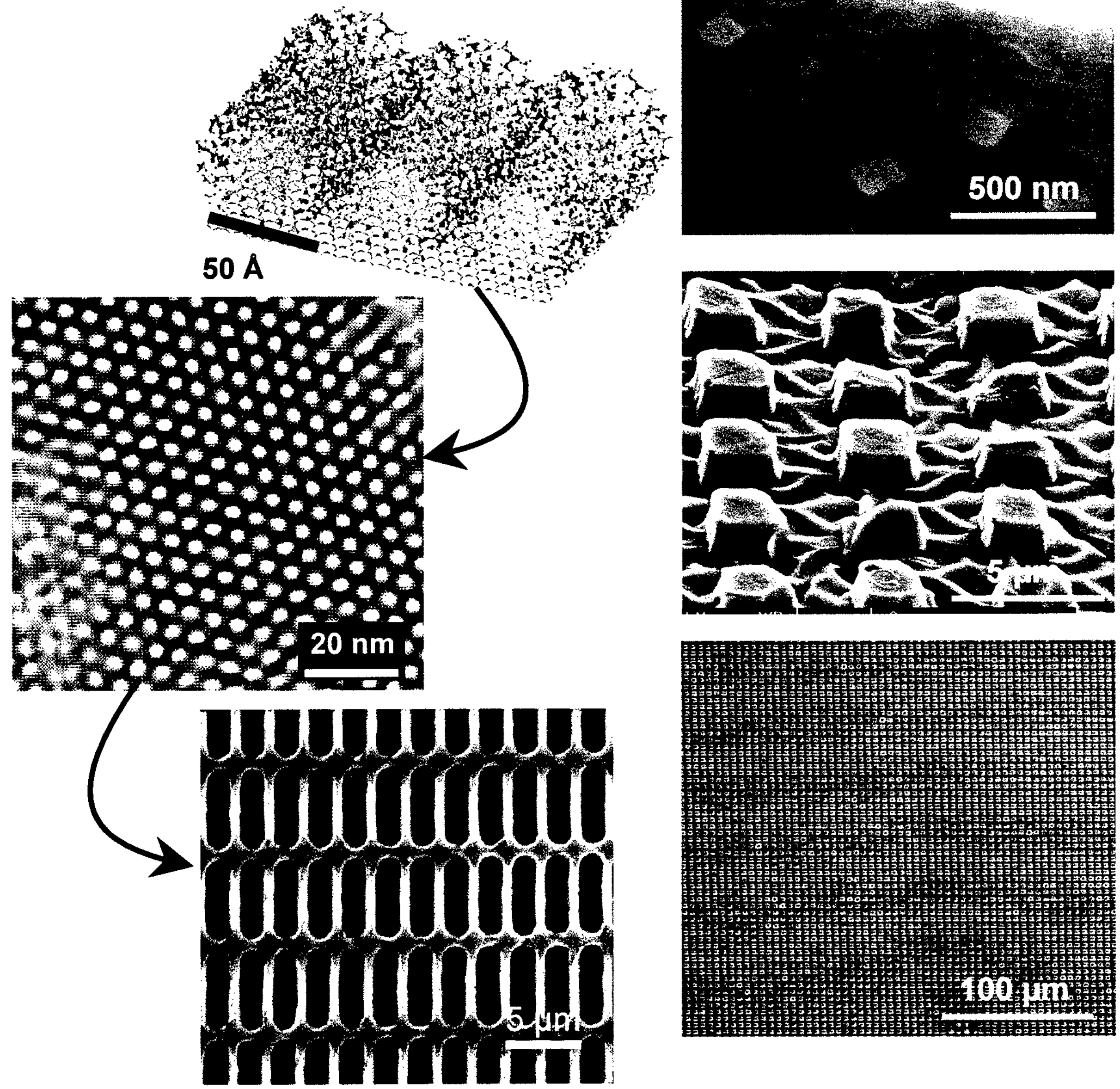
Mechanism: Film Growth at the Air-Water Interface



N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)

Liquid Crystal Templating





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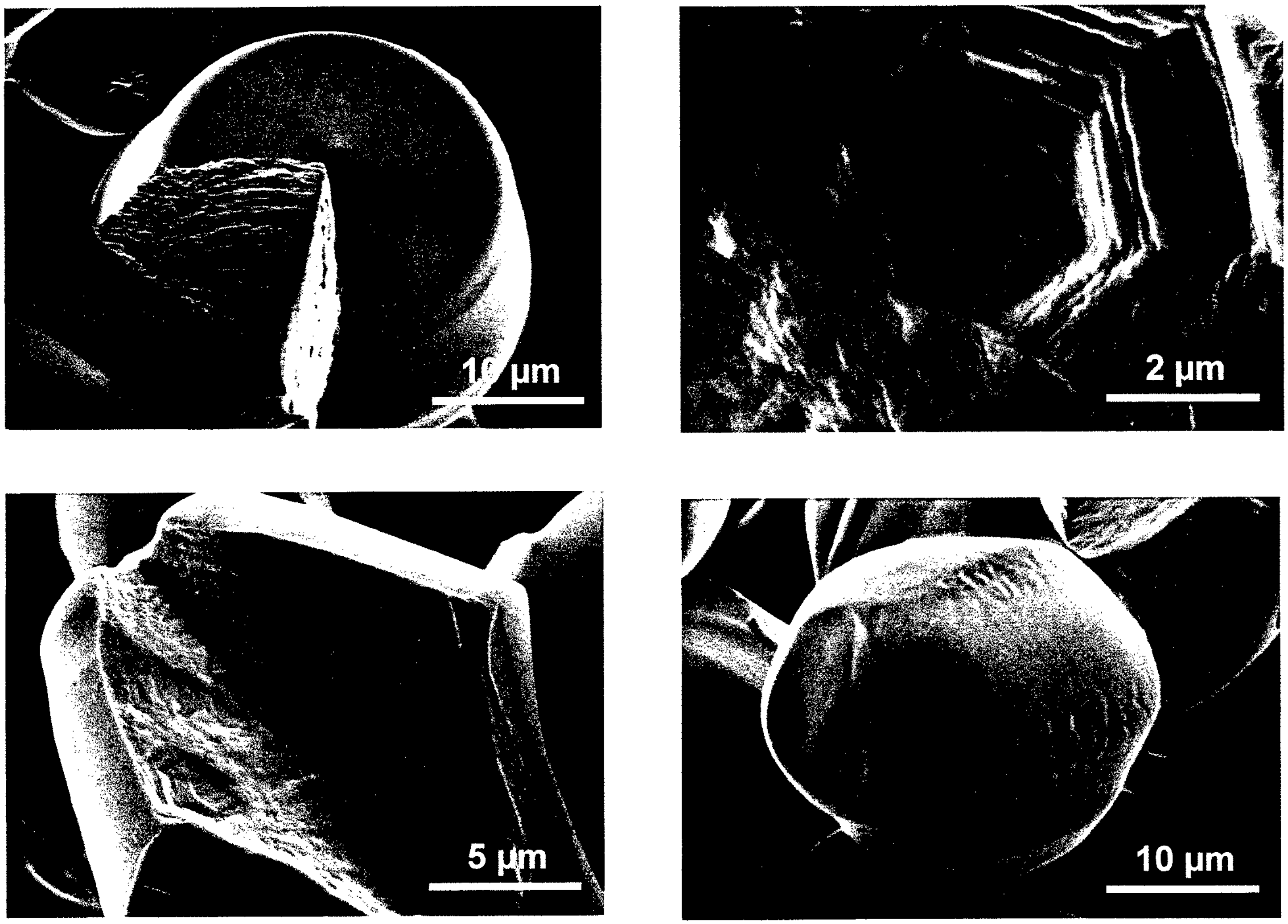
A. Y. Ku, D. A. Saville, I. A. Aksay, unpublished research (1999)

Particle Growth: Mesoscopic Crystallization



N. Yao, A. Y. Ku, H. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, submitted to *Langmuir* (1999)

Mechanism: Future Directions

- *Strategic*
  - Target mesoscopic crystallization stage
  - Use surface effects to orient nuclei

- *New approaches*
  - Apply field (E, B, shear) during mesophase formation
  - Use surface effects to influence domain orientations

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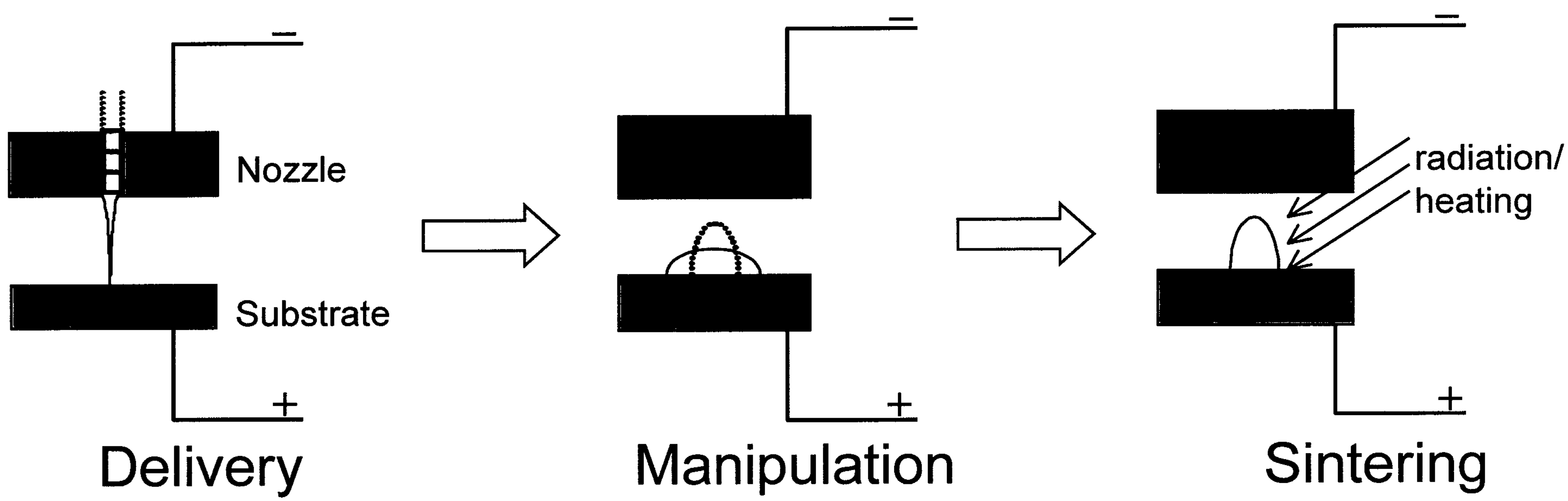
Electrohydrodynamic Printing: Cone-Jet Transition in an Electric Field

Hak Fei Poon, Dudley A. Saville,* and
Ilhan A. Aksay

*Partial support from the NSF/MRSEC (DMR 94-00362 and DMR 98-09483)

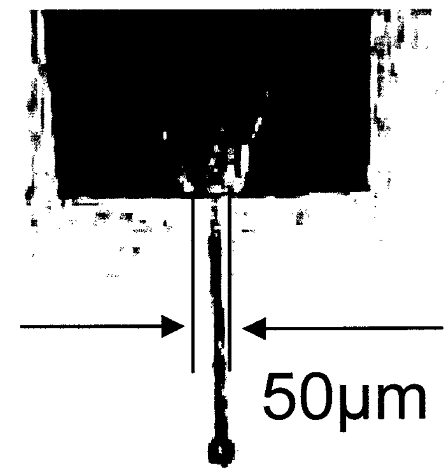
Electrohydrodynamic (EHD) Printing

- *Objective*
  - Develop a technique for microscale material decoration using electrohydrodynamic principles
- *Approach: Field-assisted flow combined with ink-jet printing*

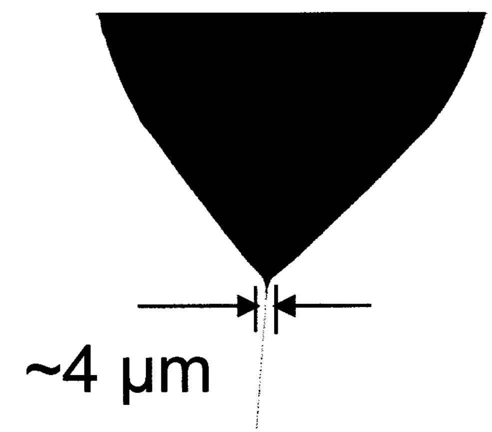


Ink Jet Technology vs. EHD Jet Printing

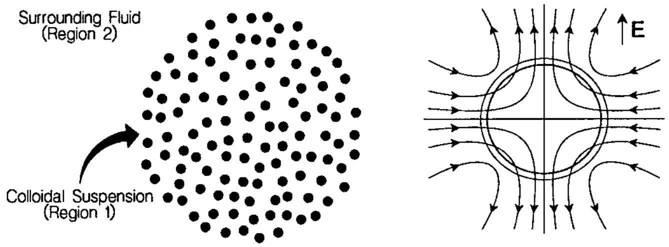
- *Inkjet technology:*
  - Resolution: 1200–1400 dpi ~ 15–20 μm
  - Drop size ~ order of channel size
  - Reducing channel size causes clogging with colloidal suspensions



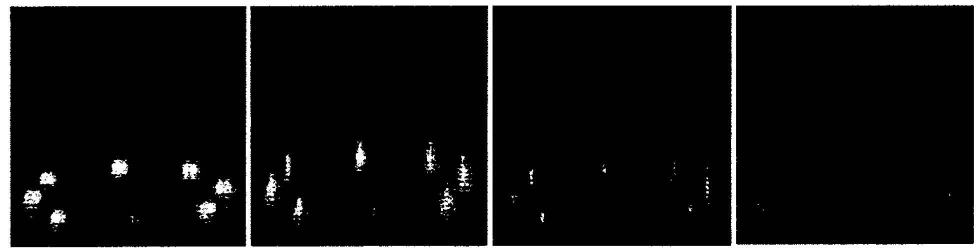
- *EHD printing*
  - Drop size ~ two orders of magnitude smaller than the channel size
  - No clogging



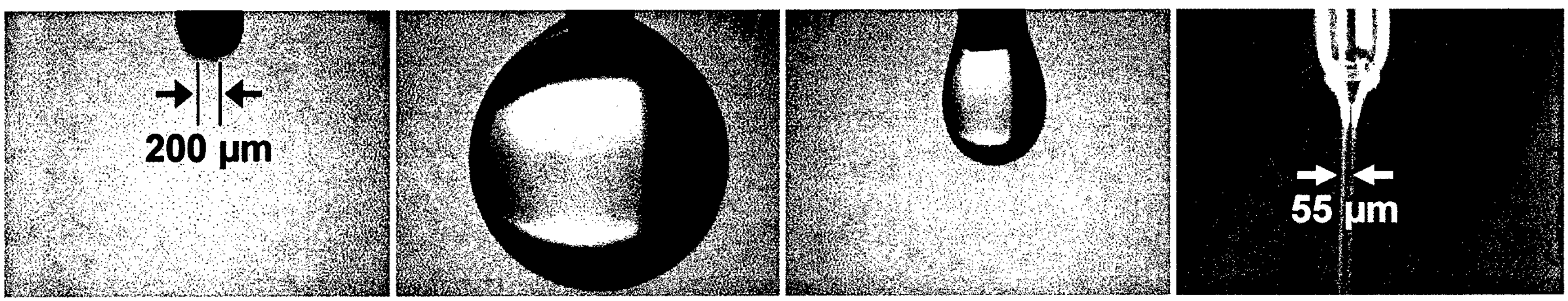
Electrohydrodynamic Printing



D. A. Saville, *Phys. Rev. Letts*. **71** (1993).

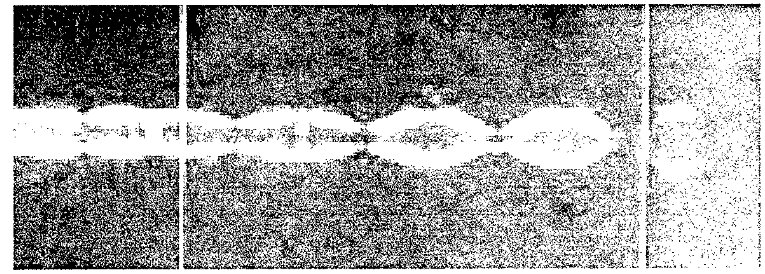


M. Trau, S. Sankaran, D.A. Saville, I.A. Aksay, *Nature* **374** 437-9 (1995);
M. Trau, S. Sankaran, D.A. Saville, I.A. Aksay, *Langmuir* **11** 4665-72 (1995).

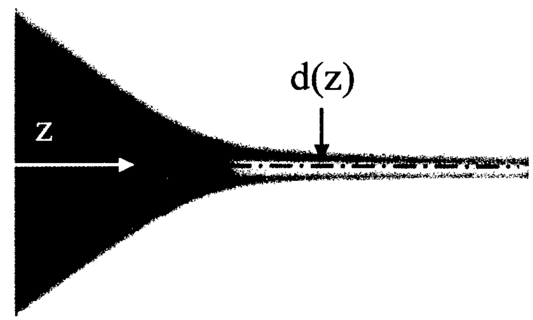


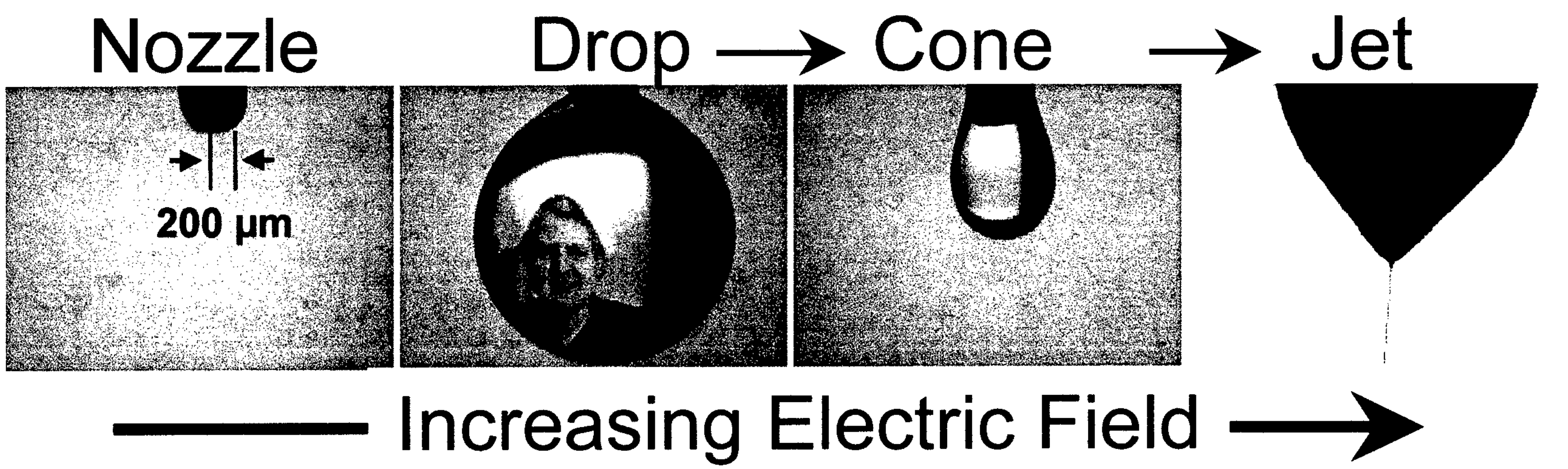
- ***Issues***
  - **Balance of interfacial tension and e-forces**
  - **Smallest diameter 100 nm (?)**
  - **Deployment, spreading, solidification -- control by e-forces shaped electrodes**
  - **Balance fluid properties with particles to produce a filament, deploy it, ...**

What is Cone-Jet Transition



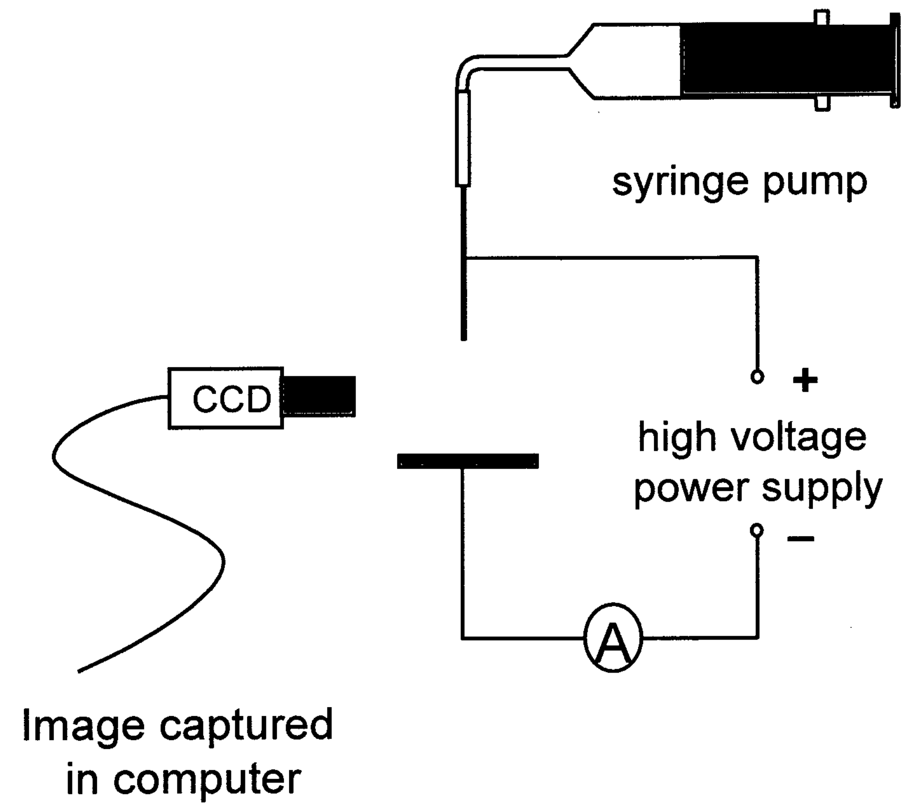
- Capillary jet instability (Rayleigh, 1878)
- Cone jet transition (Zeleny, 1915, 1917)
- Taylor's model (1964) - electrical and surface tension force
- De la Mora et al. (1993): $I \sim Q^{1/2}$, $d \sim Q^{1/3}$





Elements of the Investigation

- *Direct measurement of of jet size*
- *Re-examination of the cone jet transition*
- *Identification of a new regime where current and droplet diameter follow different scaling laws*



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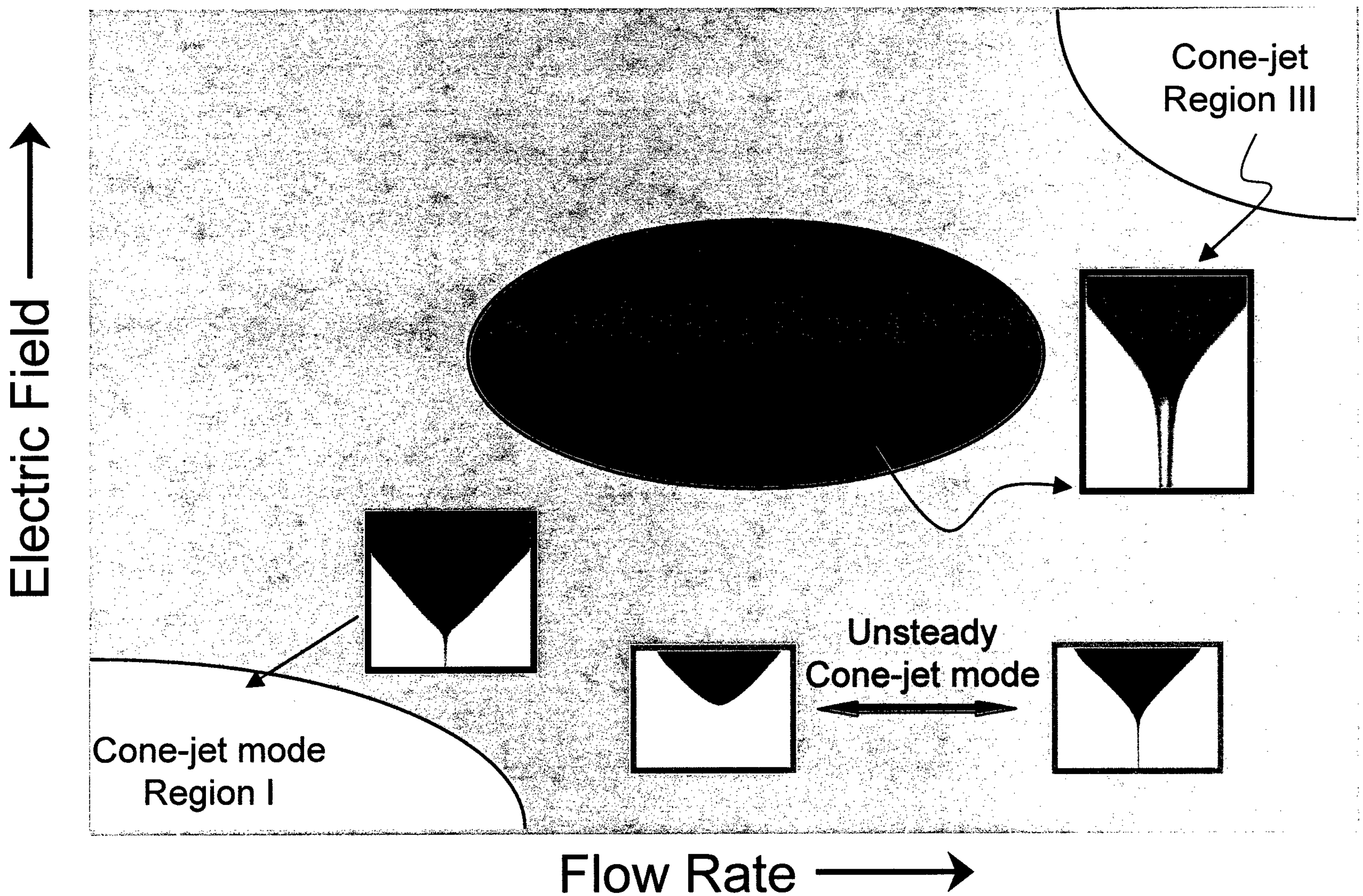
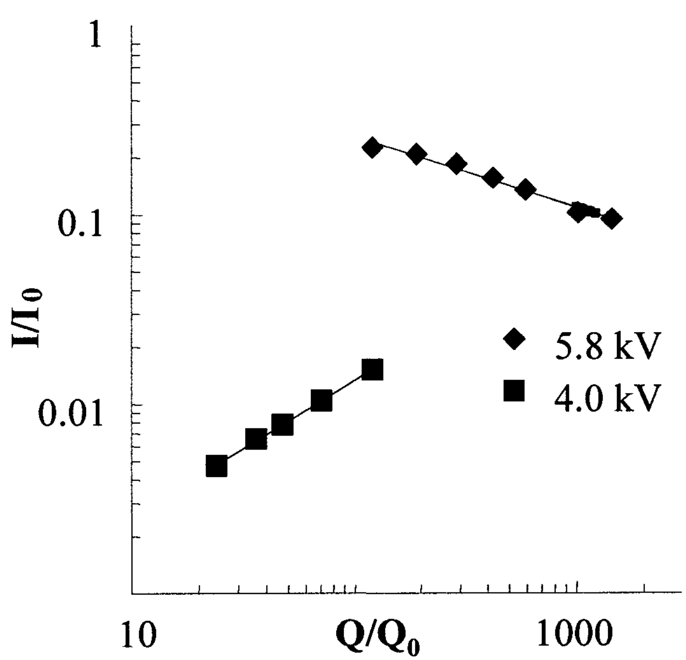
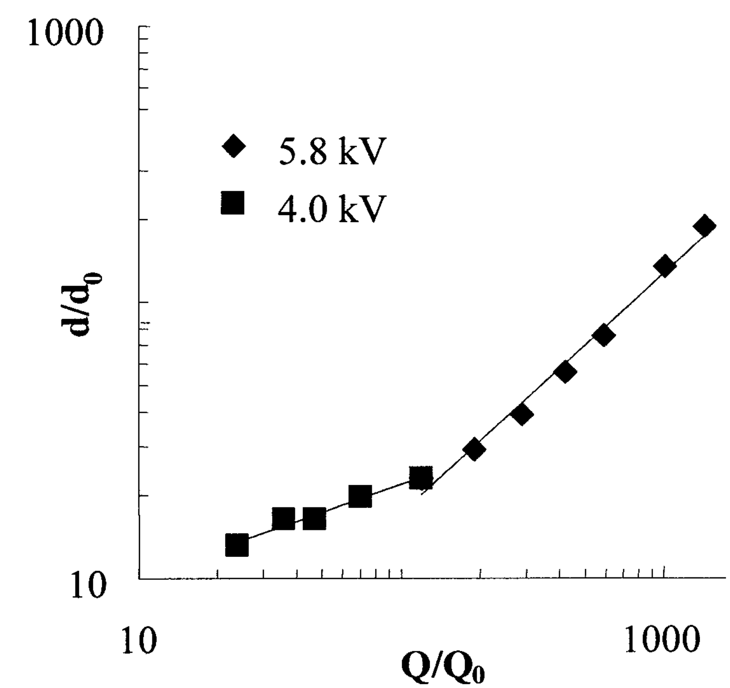
Cone-Jet Transition Phase Diagram



New Large Flow, High Current Regime

- *De la Mora's Model*
  - Low flowrate, low current regime
    $I \sim Q^{1/2}$, $d \sim Q^{1/3}$
  - Experimentally confirmed
- *New regime*
  - Large flowrate, high current regime
    $I \sim Q^{-0.3\sim0.4}$, $d \sim Q^{0.8\sim0.9}$





Discussion

- ***A Consistency Check - Scaling Analysis:***

  Convection Current: $I \sim \pi d\, u_s\, \rho_s$ - ***bulk conduction negligible***

  Surface Velocity: $u_s \sim 4Q/d^2$ - ***for a slender jet with flat velocity profile***

  Surface Charge Density: $\rho_s \sim \varepsilon\varepsilon_0 E_n^{\,0} \sim \varepsilon\varepsilon_0\, (2\gamma/\varepsilon\varepsilon_0 d_j)^{1/2}$

  $\Rightarrow I/Q \sim d^{-3/2}$

check:

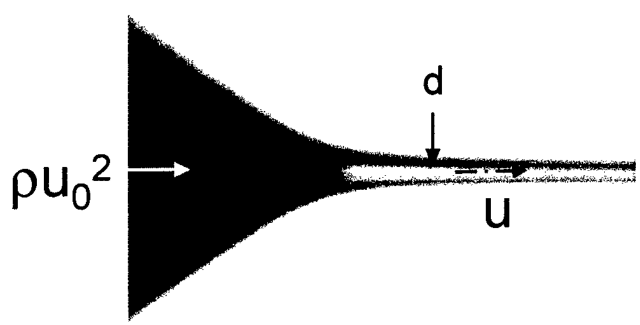
For the large flow, high current regime, take

$I \sim Q^{-0.3}$, $d \sim Q^{0.9}$

$I/Q \sim Q^{-0.3}/Q \sim Q^{-1.3} \sim (Q^{0.9})^{-3/2} \sim d^{-3/2}$

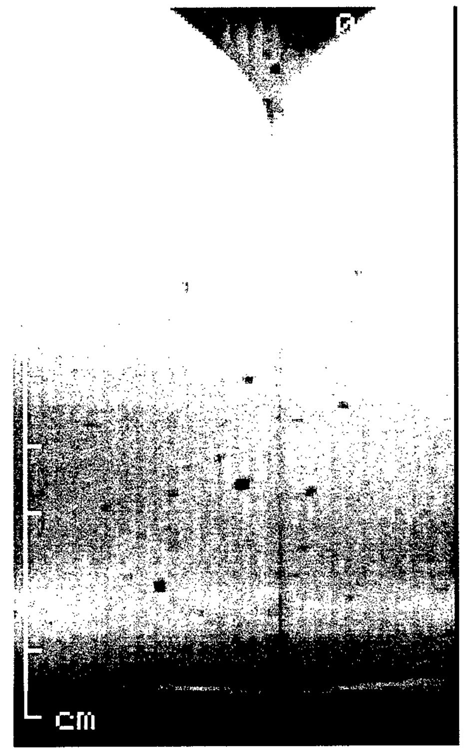
Comparison and Explanation

$u \sim Q^{\alpha}$	α	Jet diameter, $d \sim (Q/u)^{1/2}$	Comments
Delamora et al. (1993)	1/3	$d \sim Q^{1/3}$	Agree well at low flow rate when dynamic pressure at the entrance of nozzle are negligible
Ganan Calvo et al. (1994)	0	$d \sim Q^{1/2}$	
Our finding	<0	$d \sim Q^{0.9}$	Gaining significance of dynamic pressure at increased flow rate $\Rightarrow$ i) d $\uparrow$ ii) u $\downarrow$



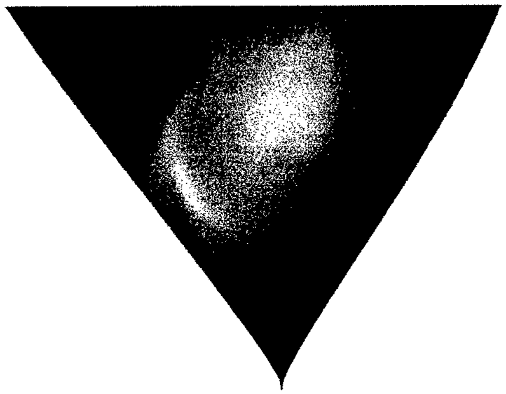
Cone-Jet Transition for Colloidal Suspension

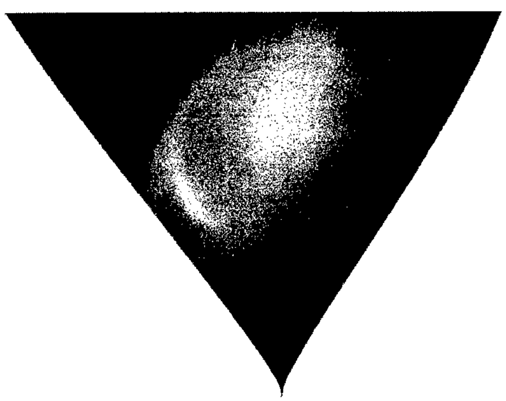
- ***Effect of Particles on***
  - Cone Jet Transition
  - Scaling Laws
  - Jet Stability
  - Buckling Issues
- ***Suspension Investigated***
  - Solvents: water, ethylene glycol, ethanol, glycerol
  - particles: alumina, barium titanate



10% Glycerol Dispersed
Alumina Jet
Impinging on the surface

Aqueous Alumina (10 vol% AKP-50)



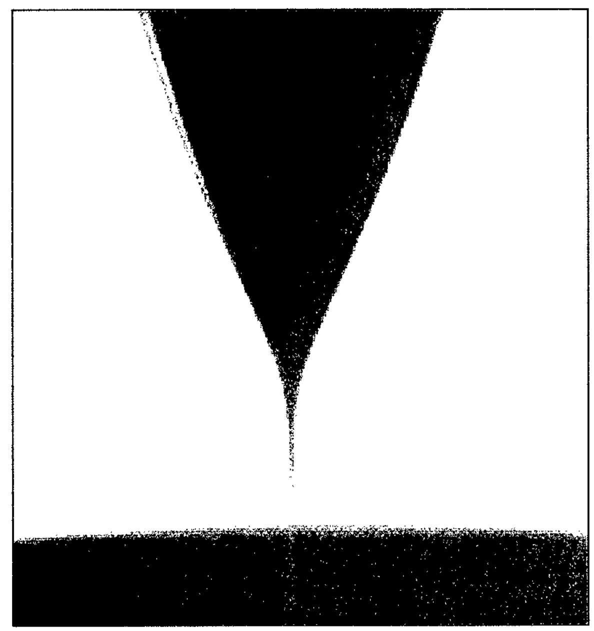


- ***Unsteady and Short Jet***
  - **Possible Causes:**
    - High conductivity (1.78mS/cm)
    - Low viscosity

Effect of Concentration

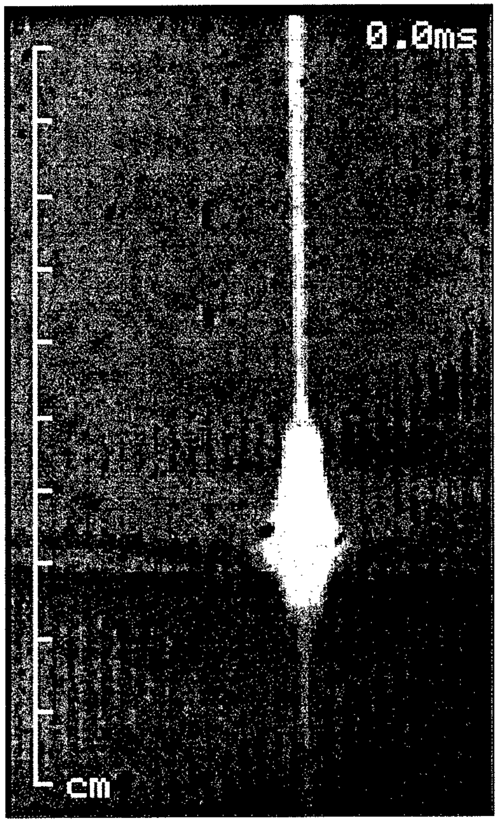
- ***Suspension prepared with water, ethylene glycol and glycerol are limited to low concentrations, typically below 20 vol%.***
- ***Higher solid loading usually results in an agglomerated suspension***

The only stable high loading suspension (up to 40 vol%) prepared thus far is alumina dispersed in ethanol.



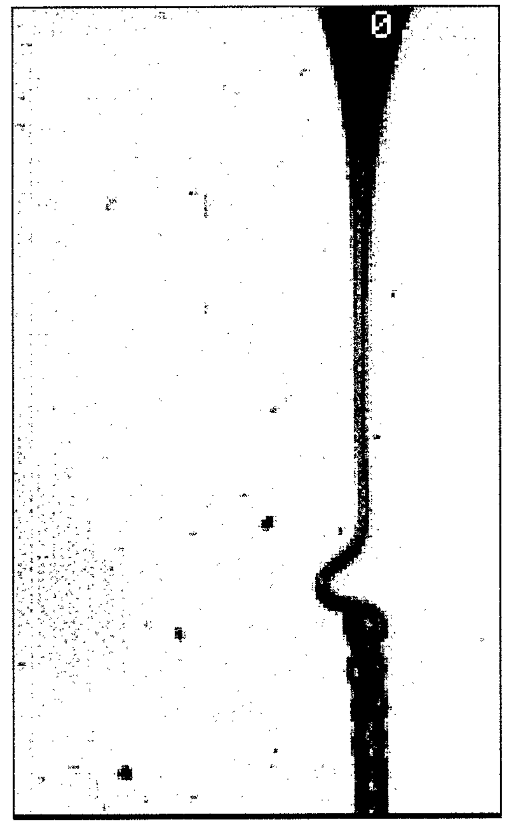
Cone-jet transition of a 37.8 vol% AKP-50 suspension dispersed in ethanol

Buckling Issues



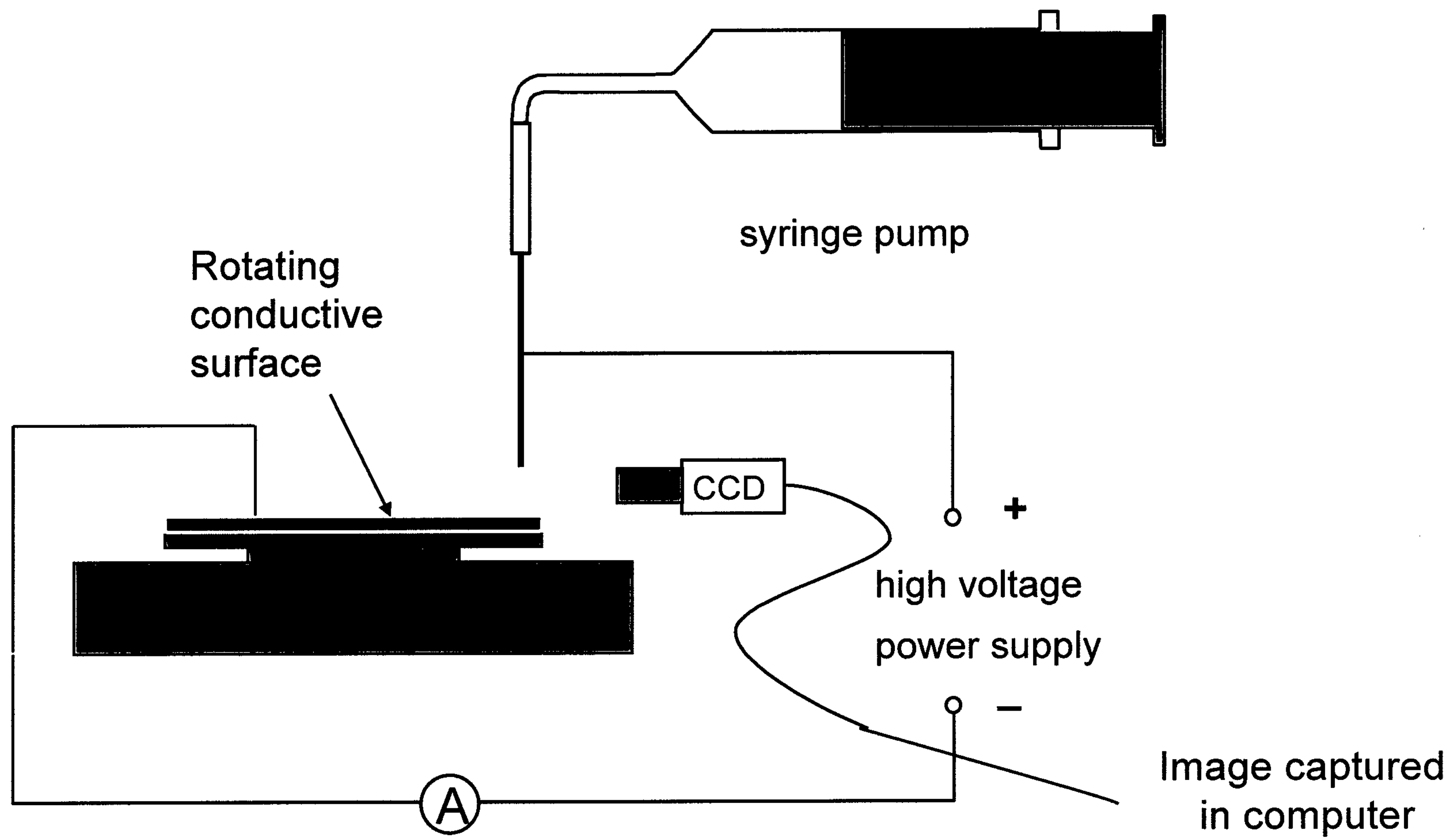
10% Glycerol dispersed alumina jet impinging on the surface

vs.



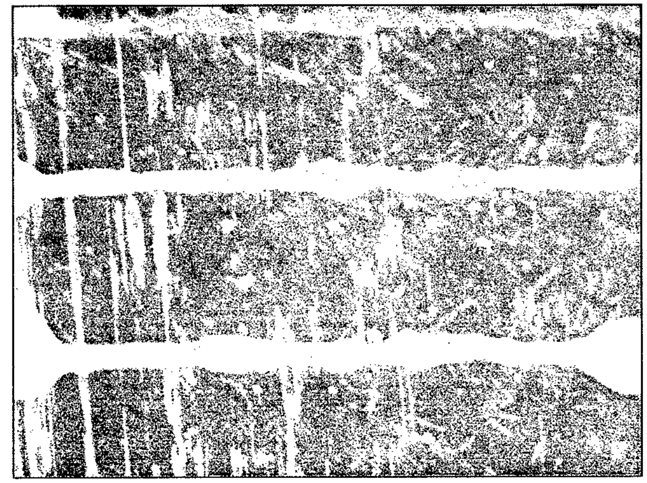
Honey jet under cone-jet domain

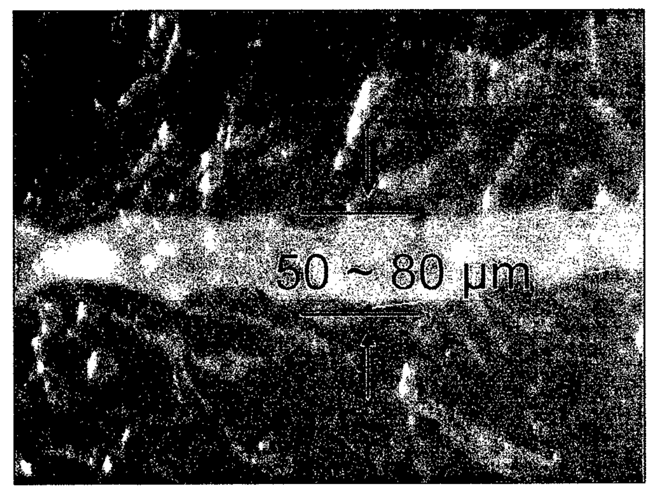
A Simple Writing Device



Line Pattern

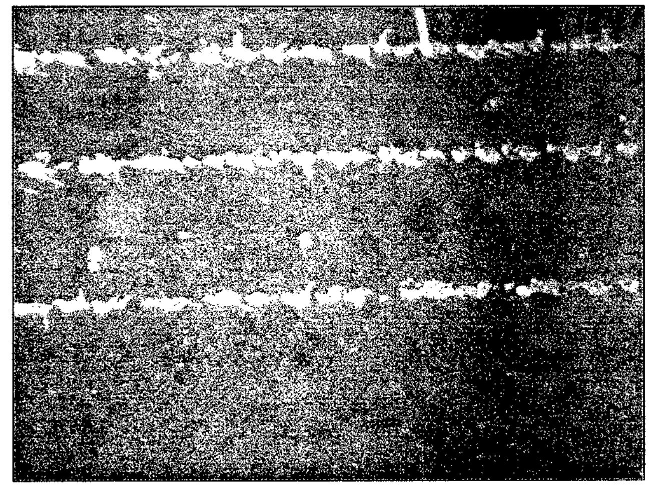
- *Operating Conditions:*
  - 10 vol% alumina suspension dispersed in glycerol
  - Jet size ~ 10 μm
  - Flow Rate ~ 2 ml/hr
  - Surface velocity ~ 0.2 m/sec
  - Substrate surface: 0.1 μm pore size filter membrane
  - Cone Base Diameter: 558 μm

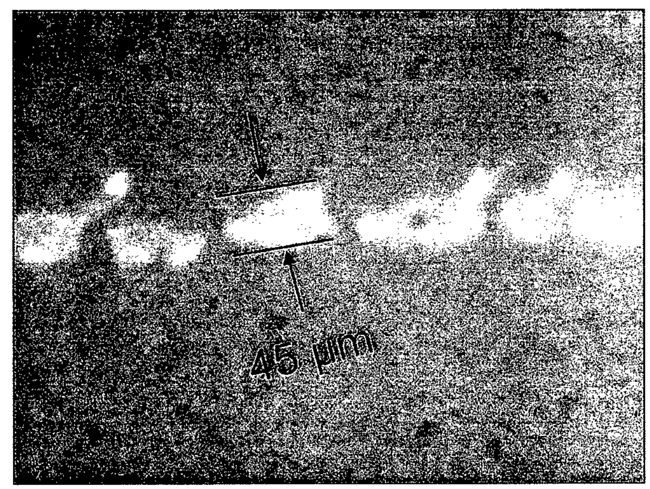




Effect of Surface Speed

- *Operating Conditions:*
  - Flow rate ~ 2 ml/hr
  - Surface velocity ~ 0.9 m/sec
  - Substrate surface: 0.1 μm pore size filter membrane
  - Jet size: 10 μm
- *Increase in surface moving speed leads reduce line thickness*
- *Rayleigh instability is enlarged at such small scale*





Conclusions

- *Developed simple writing device*
- *Demonstrated a cone-jet domain for colloidal suspension*
- *Demonstrated the feasibility of EHD jet printing as a novel patterning technique for both homogeneous solution and colloidal suspension*
- *Current experiment configuration allowed laying down of continuous 50 - 80 micrometer suspension filament with a large orifice (OD: 558 μm, ID: 300 μm)*

Future Work

- *Scale down nozzle to produce micron-size filaments*
- *Improve writing device design to lay down micron-size filament on a surface*
- *Match jet speed and the surface speed*
- *Develop scaling laws for cone-jet transition in colloidal suspensions*
- *Characterize particle aggregation within the filament*
- *Surface wetting and dewetting issues*

Department of Chemical Engineering and
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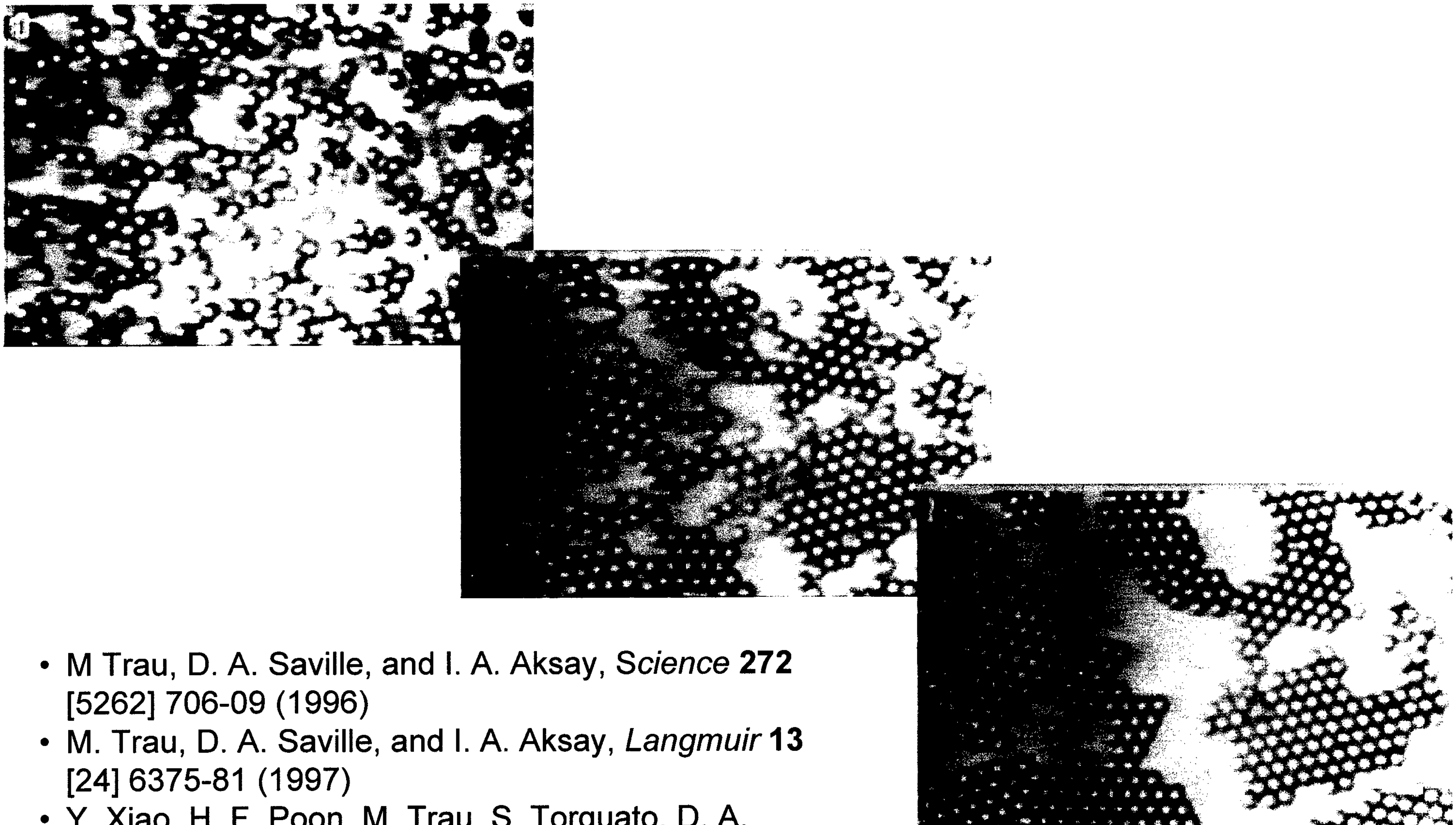
Princeton University

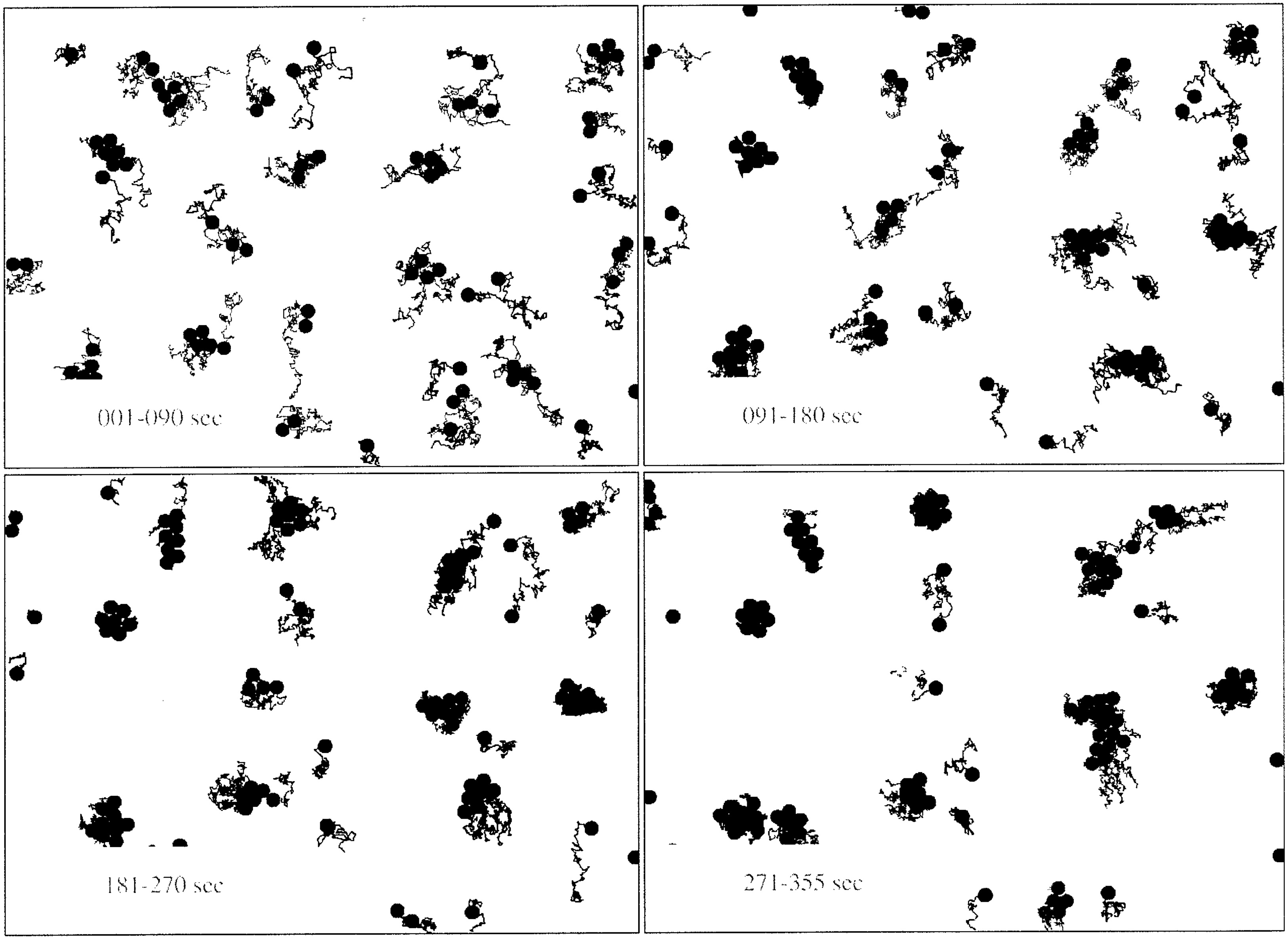
Micropatterned Colloidal Crystals: Modulation by UV-light during Electrophoretic Deposition

Ryan C. Hayward, Dudley A. Saville,* and
Ilhan A. Aksay

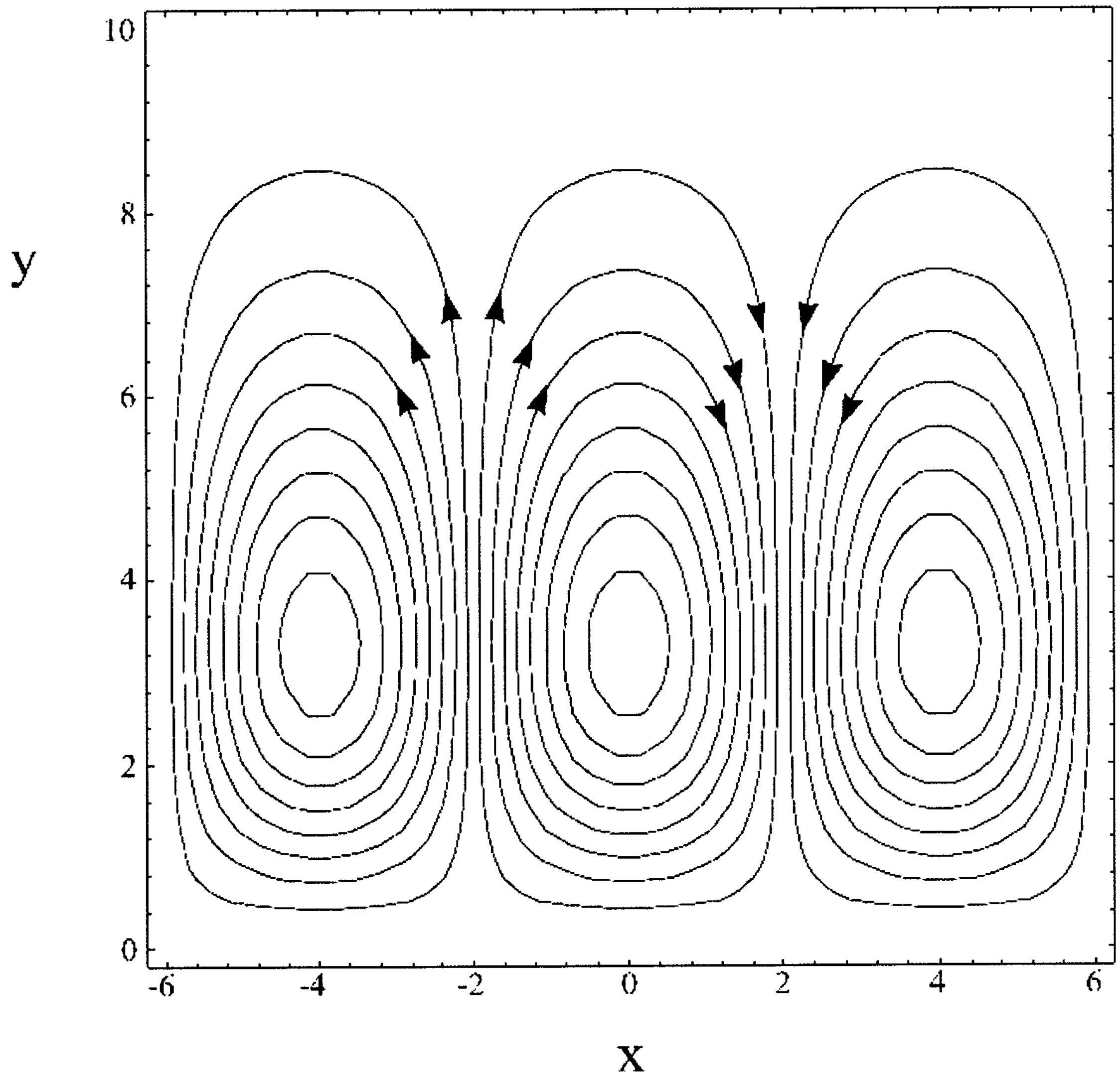
*Partial support from the NSF/MRSEC (DMR 94-00362 and DMR 98-09483)



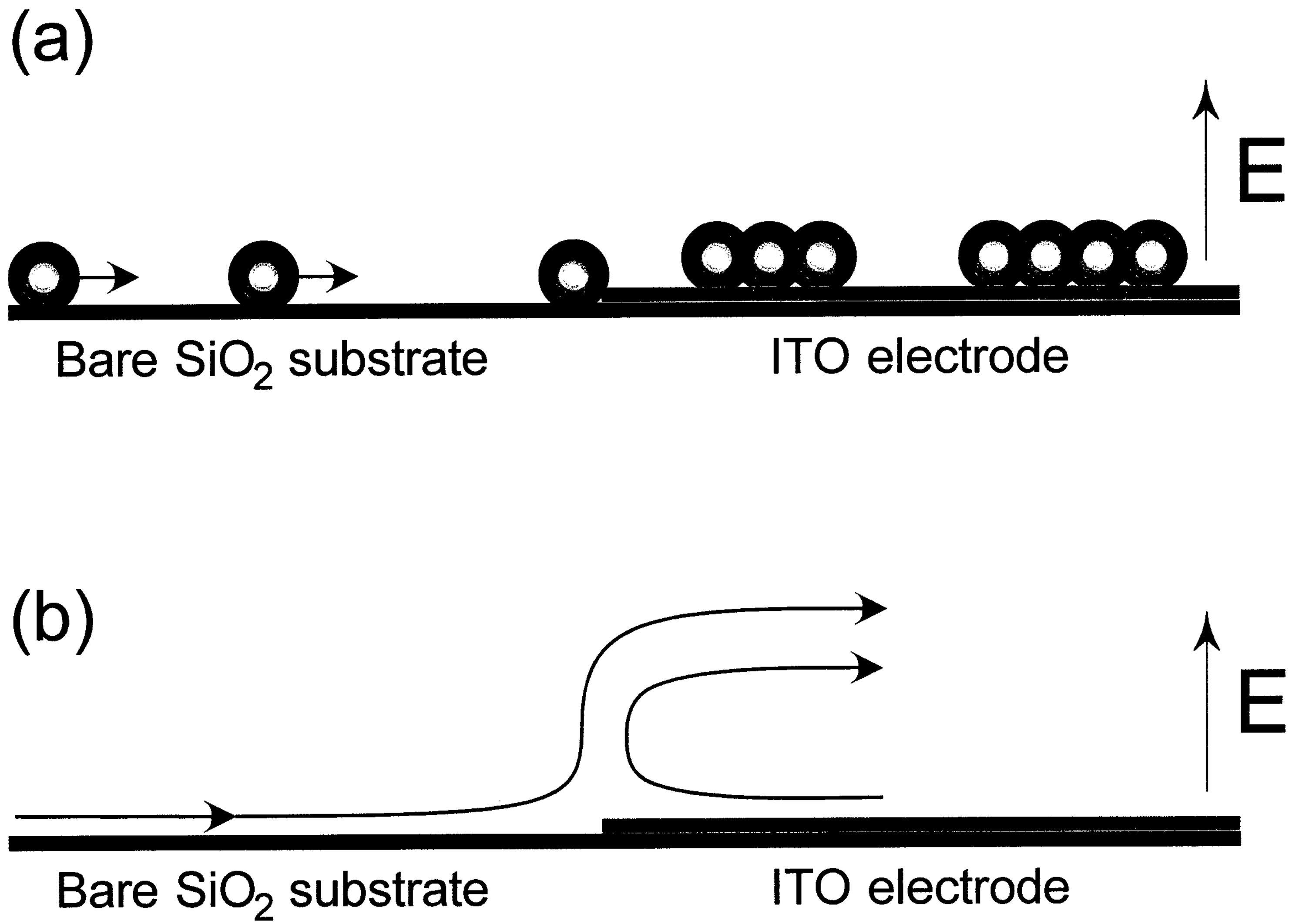
- M Trau, D. A. Saville, and I. A. Aksay, *Science* **272** [5262] 706-09 (1996)
- M. Trau, D. A. Saville, and I. A. Aksay, *Langmuir* **13** [24] 6375-81 (1997)
- Y. Xiao, H. F. Poon, M. Trau, S. Torquato, D. A. Saville, and I. A. Aksay, *Langmuir* (submitted, 1999)



Y. Xiao, H.-F. Poon, M. Trau, S. Torquato, D. A. Saville, and I. A. Aksay, *Langmuir* (submitted, 1999)

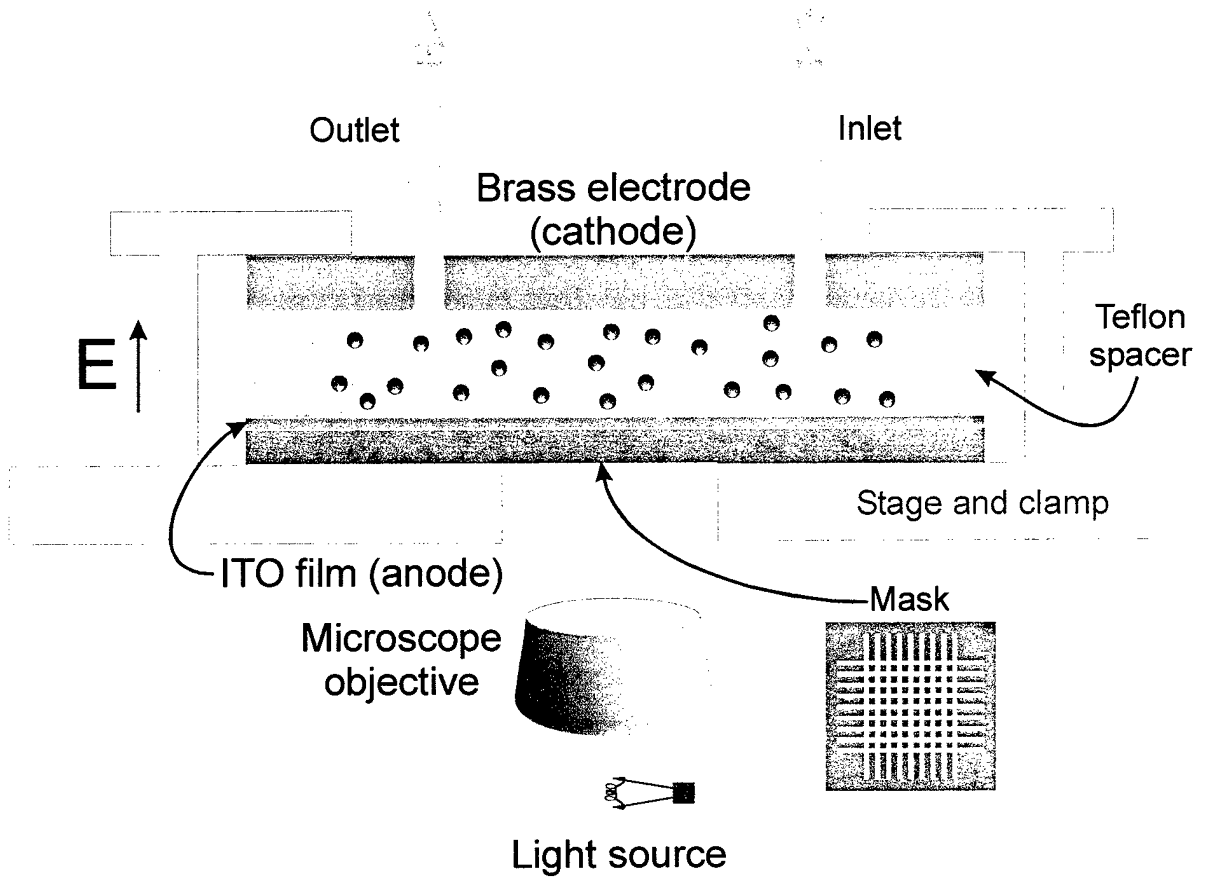


M. Trau, D. A. Saville, and I. A. Aksay, *Langmuir* **13** [24] 6375-81 (1997)



M. Trau, D. A. Saville, and I. A. Aksay, *Langmuir* **13** [24] 6375-81 (1997)

Light-Modulated Electrophoretic Deposition

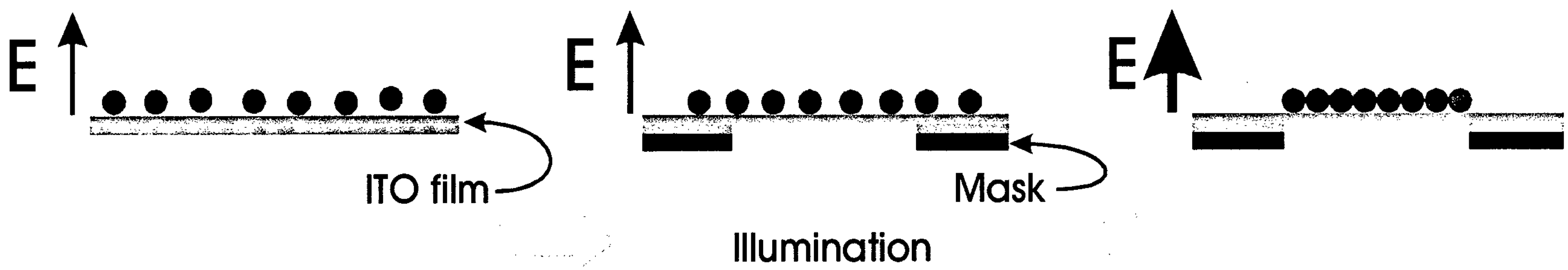


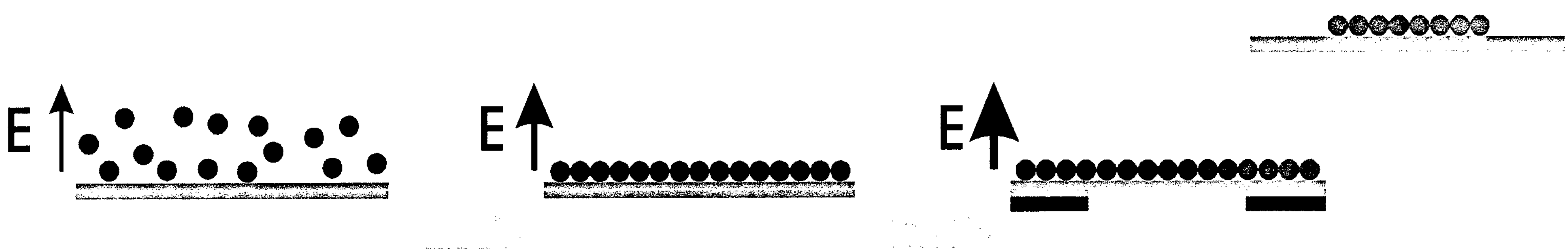
Schematic of apparatus

R. C. Hayward, D. A. Saville, and I. A. Aksay, submitted to *Nature* (1999)

Pattern Formation

Patterned assembly followed by fixing to substrate

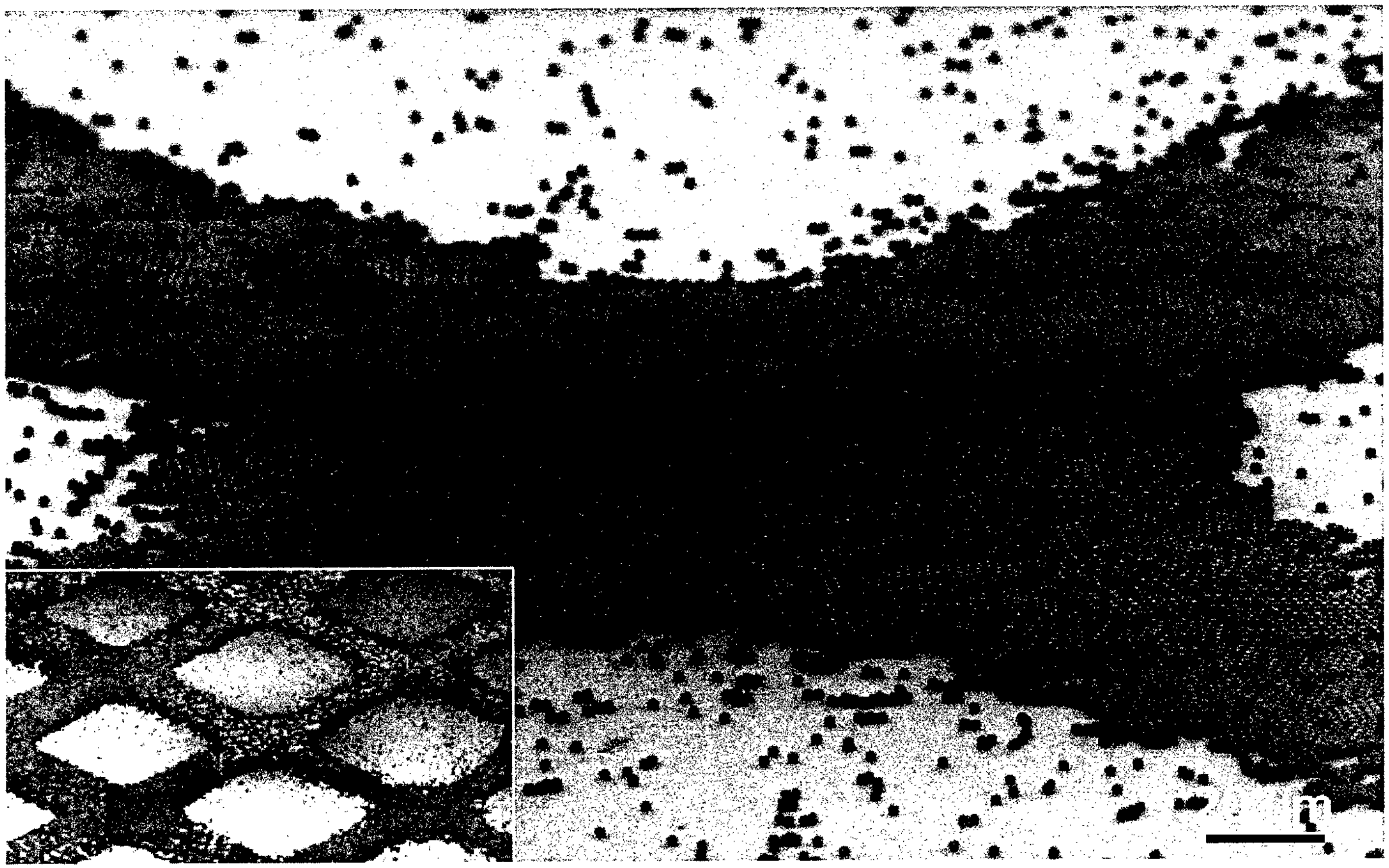




General assembly followed by patterned fixing to substrate

R. C. Hayward, D. A. Saville, and I. A. Aksay, submitted to *Nature* (1999)

Patterning of Colloidal Particles



R. C. Hayward, D. A. Saville, and I. A. Aksay, submitted to *Nature* (1999)

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

The Sponge Phase: Synthesis and Characterization

SOL M. GRUNER[‡], KAREN J. EDLER[‡], DANIEL M. DABBS[§,#], NAN YAO[#], AARON RABINOVITCH[‡], AKIN AKINC[‡], ROBERT K. PRUD'HOMME[§,#], AND ILHAN A. AKSAY[§,#]

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FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

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The "Sponge" Phase
(and other mesoporous materials)
Synthesis and Characterization

S. M. Gruner,* K. J. Edler,* D. M. Dabbs,‡
E. Hutchins,* K. M. McGrath,† and I. A. Aksay‡

*Physics, Cornell University,
Ithaca, New York 14850

‡Chemical Engineering and §Princeton Materials Institute,
Princeton University, Princeton, New Jersey 08540

†Chemistry, University of Otago,
New Zealand

Collaborators: L. Fetters, P. Wright, C. Ober, and X. Li

Supported by ARO/MURI under grant DAAH04-95-1-0102

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Ideally Mesoporous Materials

- *Contain well-defined three-dimensional network of pores*
- *Self-assemble via hydrophilic-hydrophobic interactions of the constituents, with possible subsequent processing which preserves form*
- *Have pore dimensions and structure which can be varied at will during synthesis*
- *Allow further formation of composites for applications*

Goals

- *To understand mesoporous materials formation and properties, including materials to vary:*

  1. Chemical properties
  2. Physical properties
  3. Degree to which part of the structure can be removed
  4. Synthesis pathways

Potential Applications

- *Low index optical and electronic materials*
- *Filtration media*
- *Nano-composites*
- *Encapsulation of proteins and macromolecules*
- *Catalysts and catalyst supports*
- *Osmotic membranes*
- *Selective liquid barriers*
- *Super-capacitors*
- *Heavy metal and pollutant sponges*
- *Insulation*
- *...*

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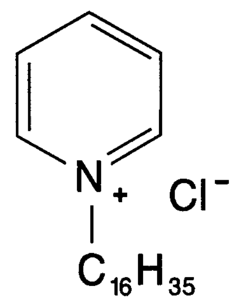
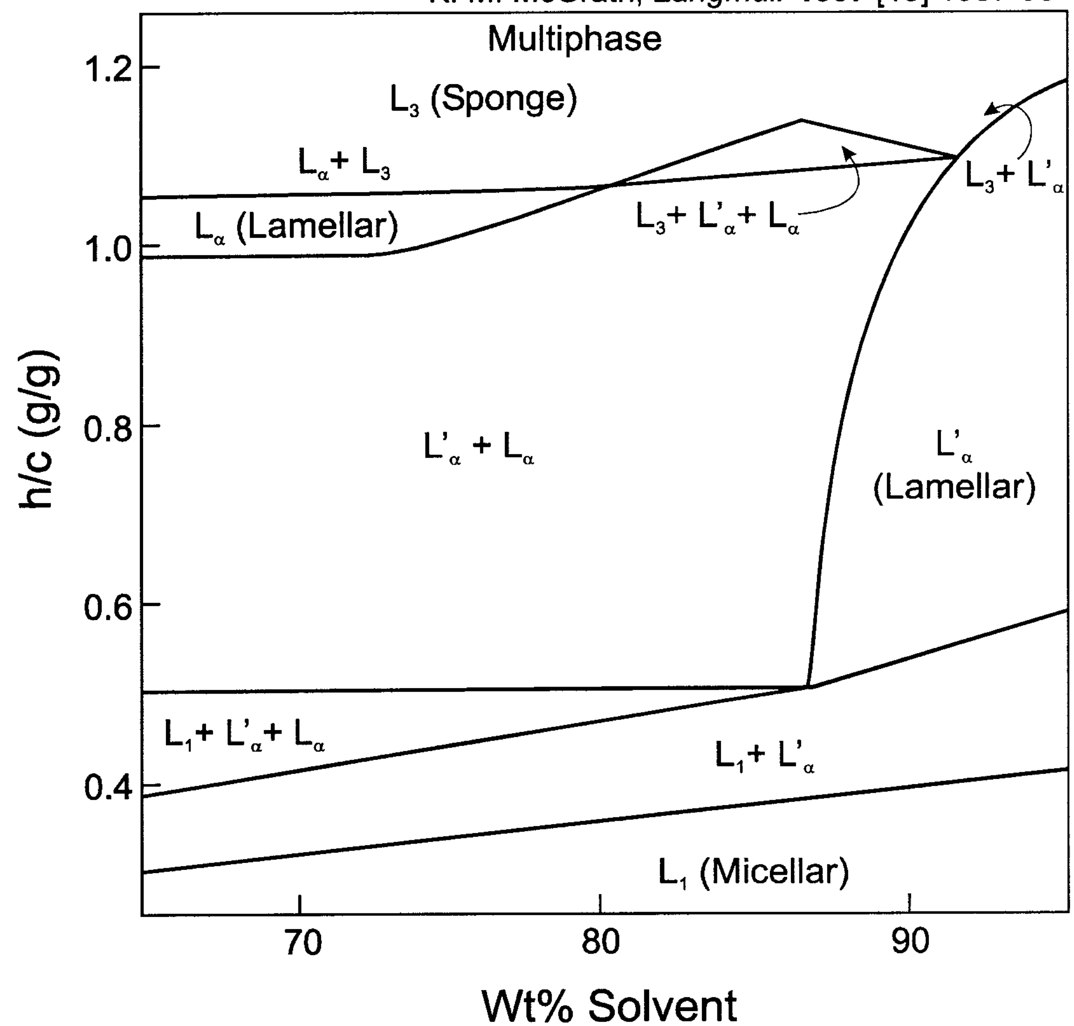
L_3 Phase

- **Cationic surfactant: cetylpyridinium chloride (CpCl)**



- **Cosurfactant: hexanol ($C_6H_{13}OH$)**
- **Solvent (aq. HCl) ranges from 55 to 95% by weight**
  - yields pores of 5 to 100 nm, scaled to solvent content

K. M. McGrath, *Langmuir* **1997** [13] 1987-95



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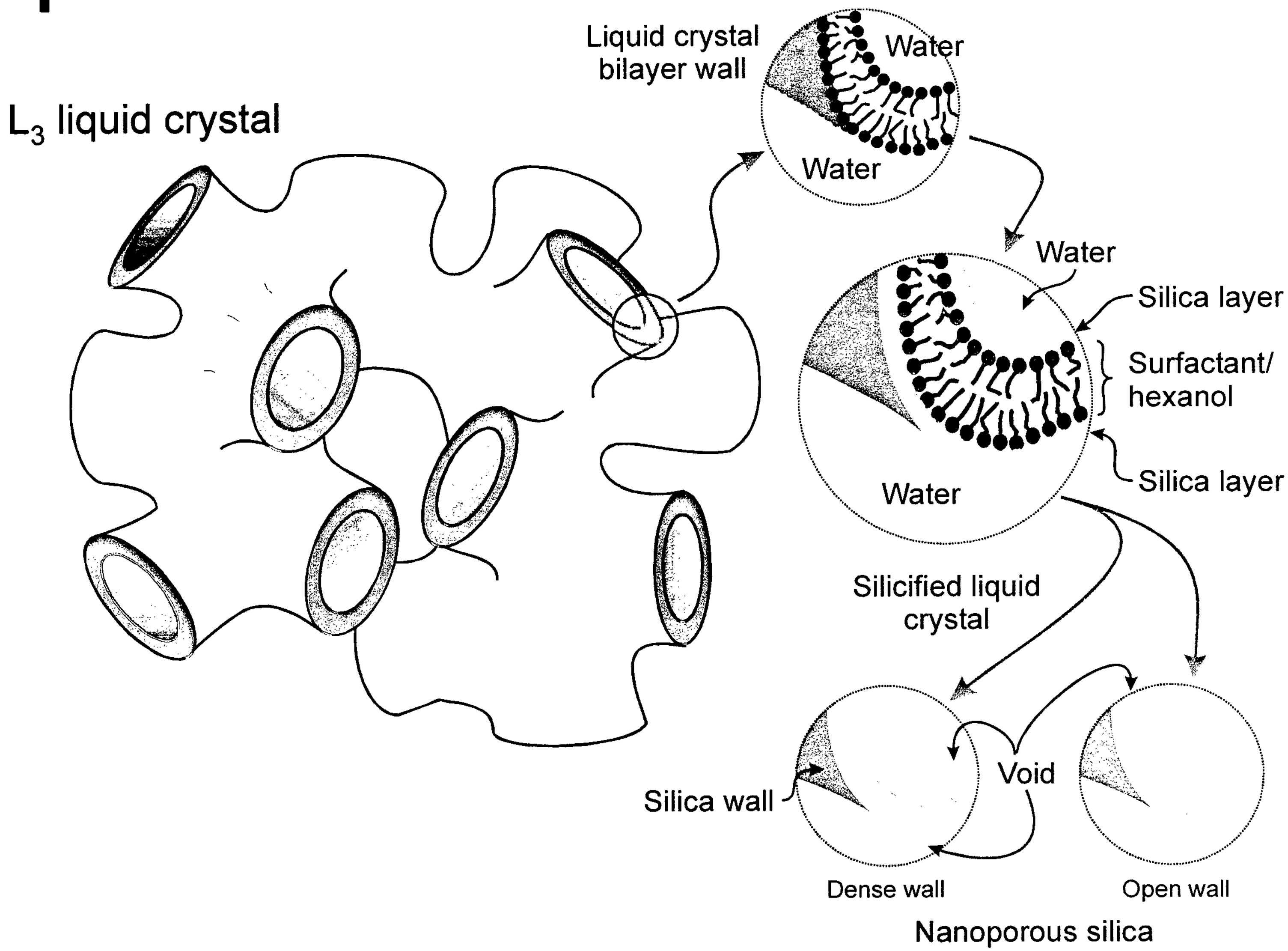
Templation and Extraction



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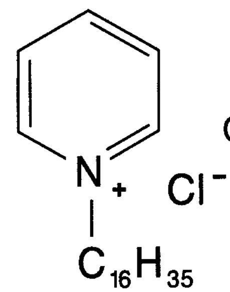
Procedure

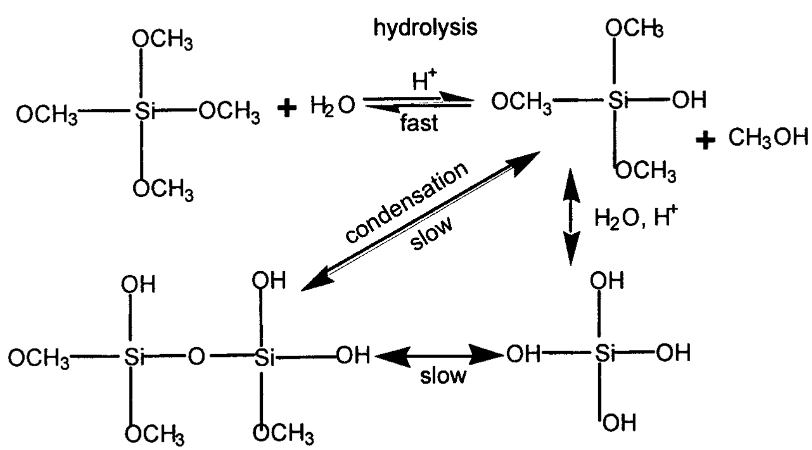
hexanol and cetylpyridinium chloride + 0.2M HCl (aq) → L_3 solution → Addition of TMOS → Gelation → [redacted]

[redacted] → [redacted] / [redacted] → [redacted]

water →

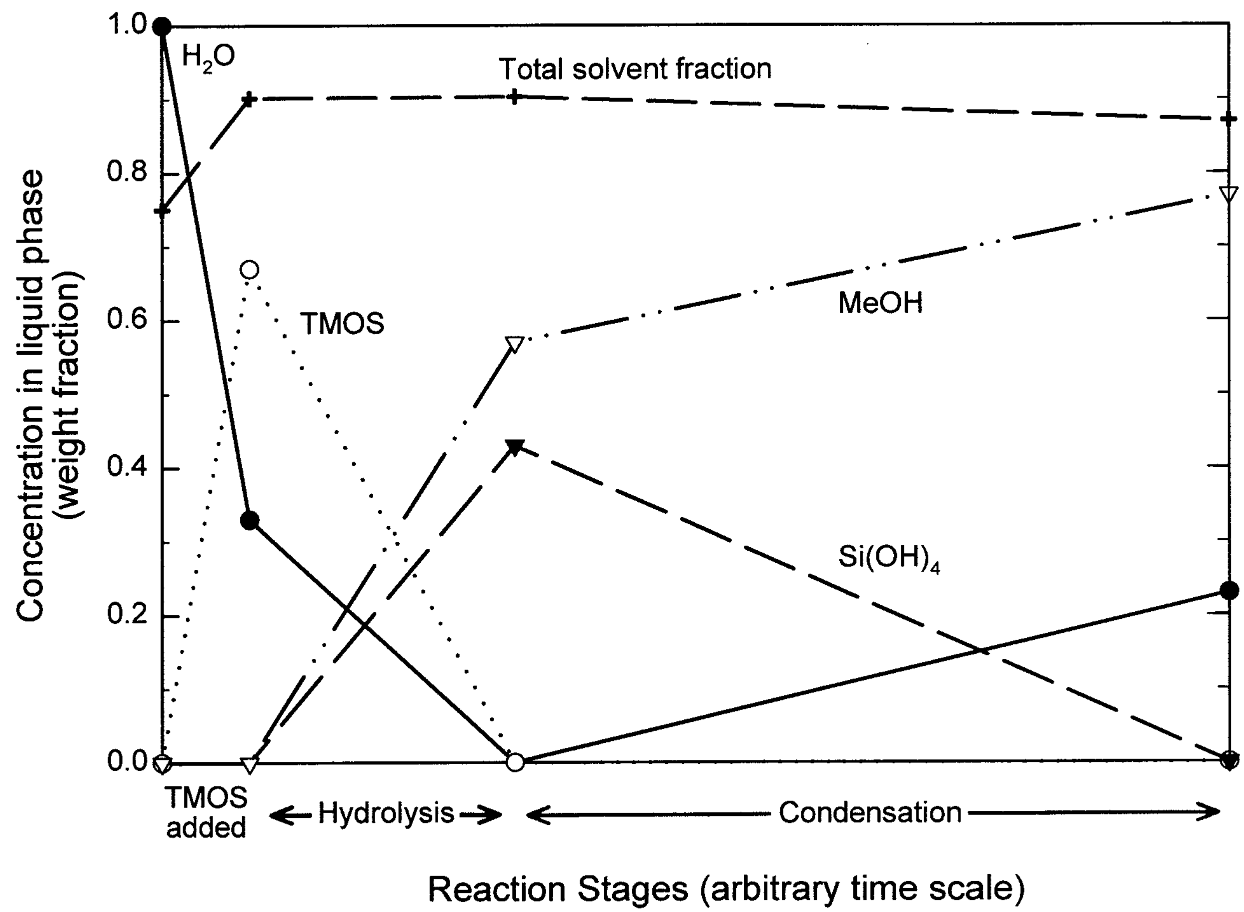


Cetylpyridinium chloride



Changes in the Liquid Phase during Templating

- Adding TMOS raises solvent fraction in L_3 solution
- Hydrolysis removes water, adds methanol to the liquid phase
- Condensation returns water to liquid phase
- Final effective solvent fraction greater than initial



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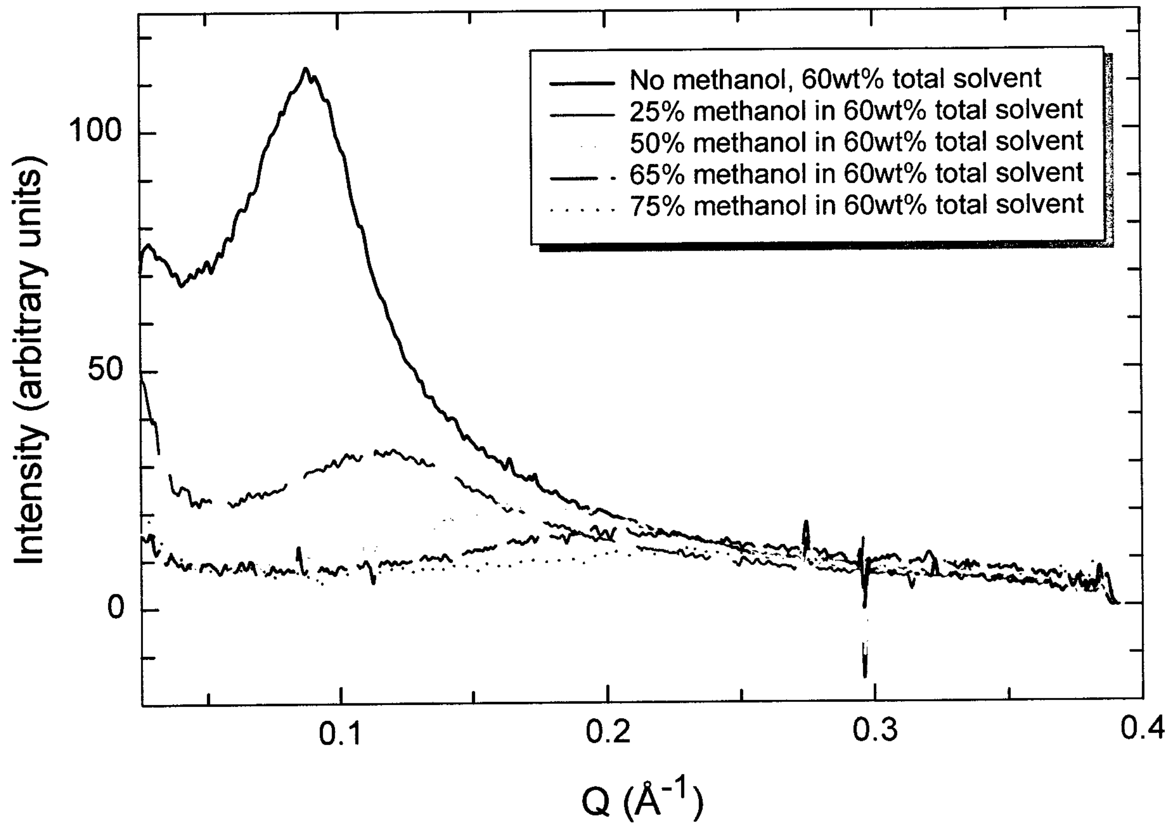
Effect of Methanol on L_3 Liquid Crystal

- Hydrolysis of TMOS produces methanol
- Increasing methanol content in solution roughens surface of bilayer and expands bilayer surface area
- Competing processes:
  - dissolution of liquid crystal
  - condensation of TMOS on surfaces



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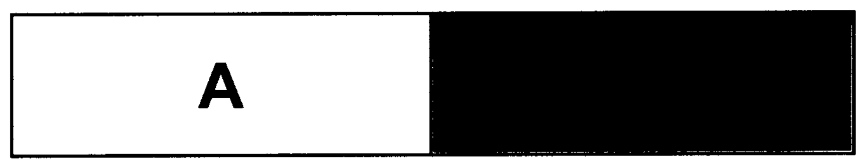
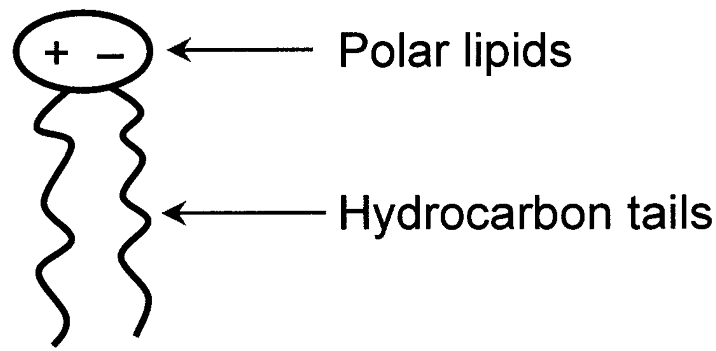
Generalized Amphiphile

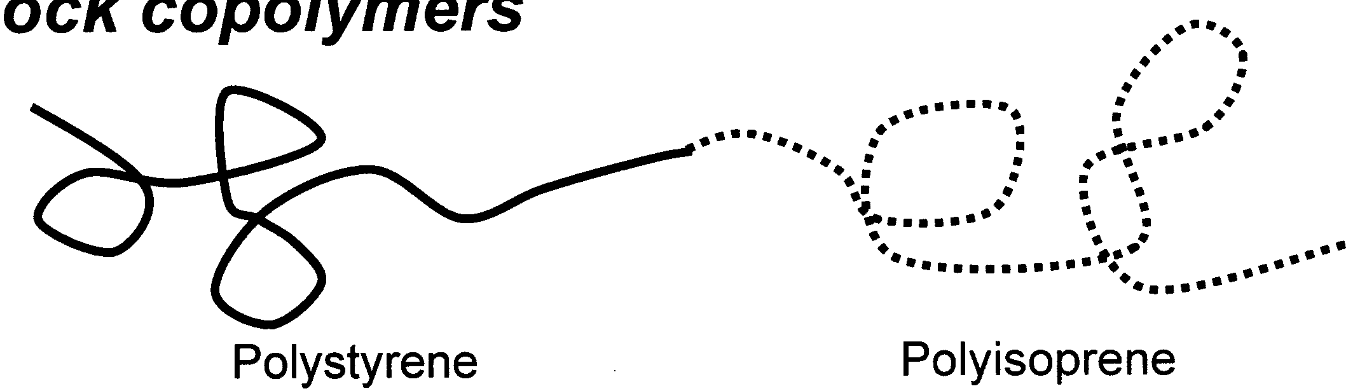


Where A & B do not mix

- ***Surfactants***
  - **Detergents**
  - **Soaps**
  - **Biomembrane lipids**



- ***Block copolymers***



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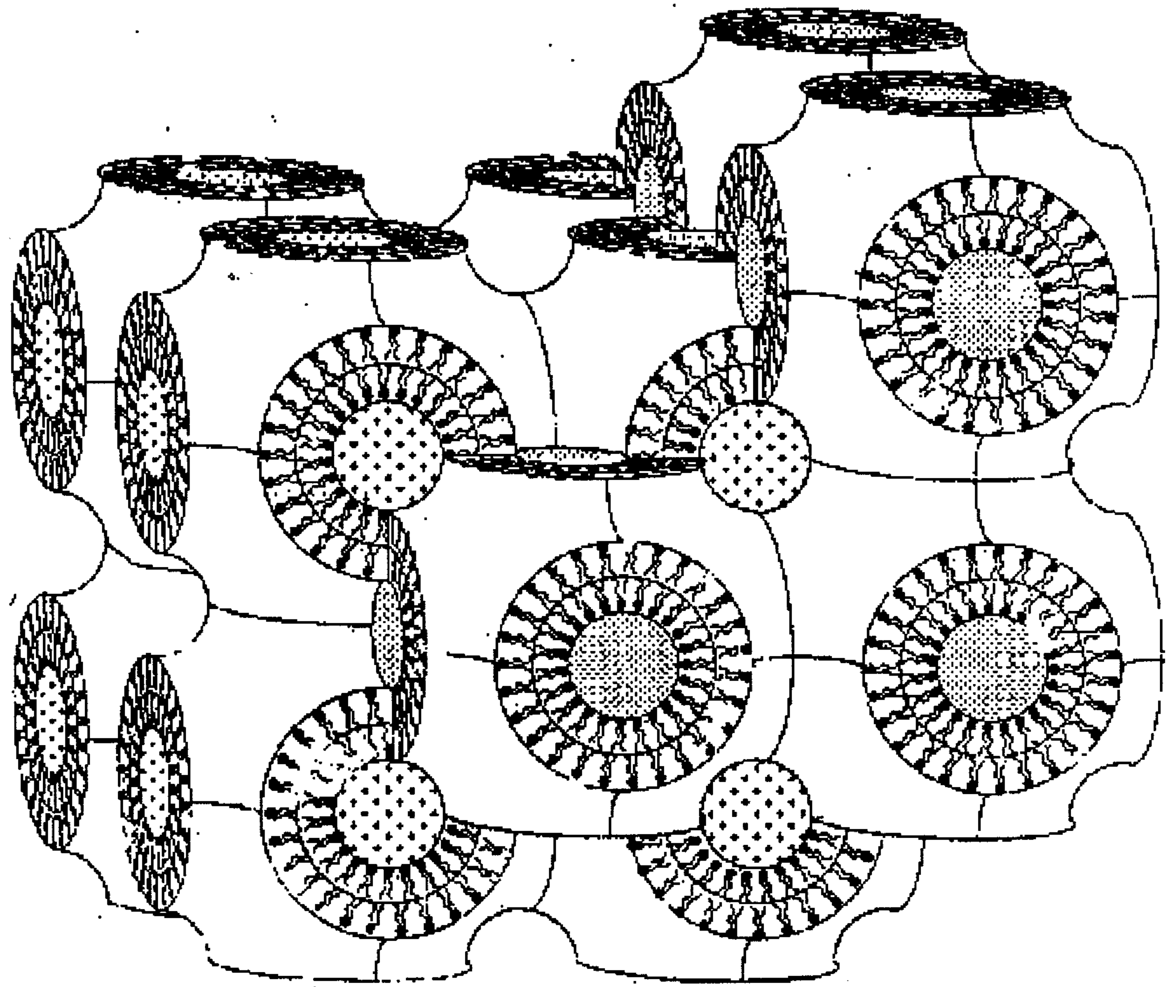
Plumber's Nightmare ($Ia\bar{3}d$)



Tate *et al.*, *Chem. Phys. Lipids* **57** (1991) 147

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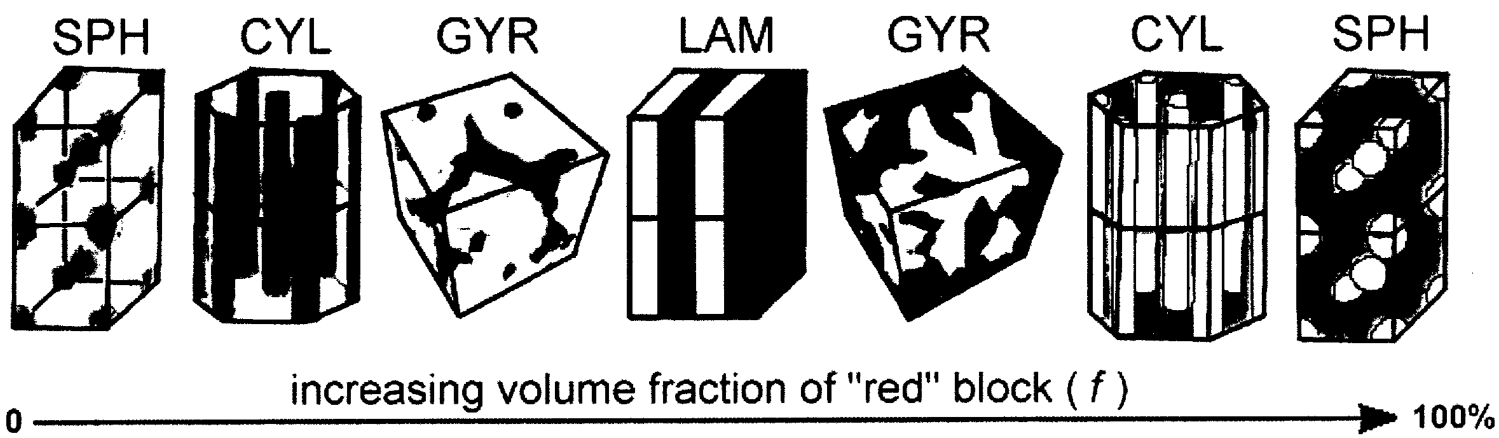
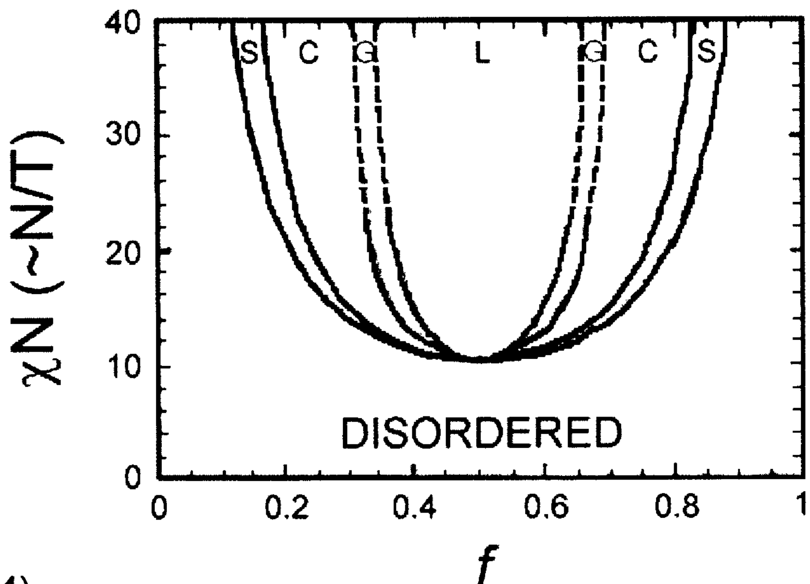
Block Copolymer Phase Behavior





Matsen and Schick (1994)

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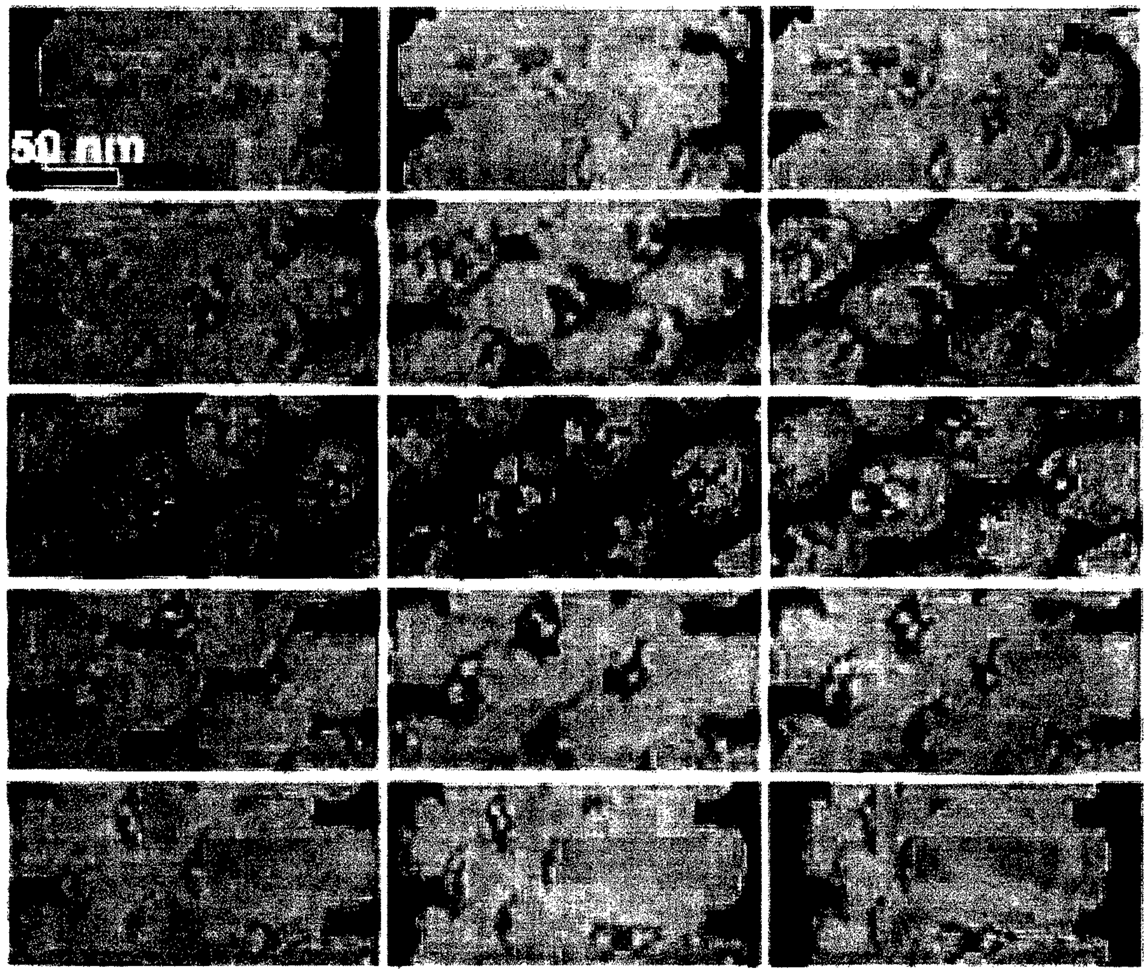
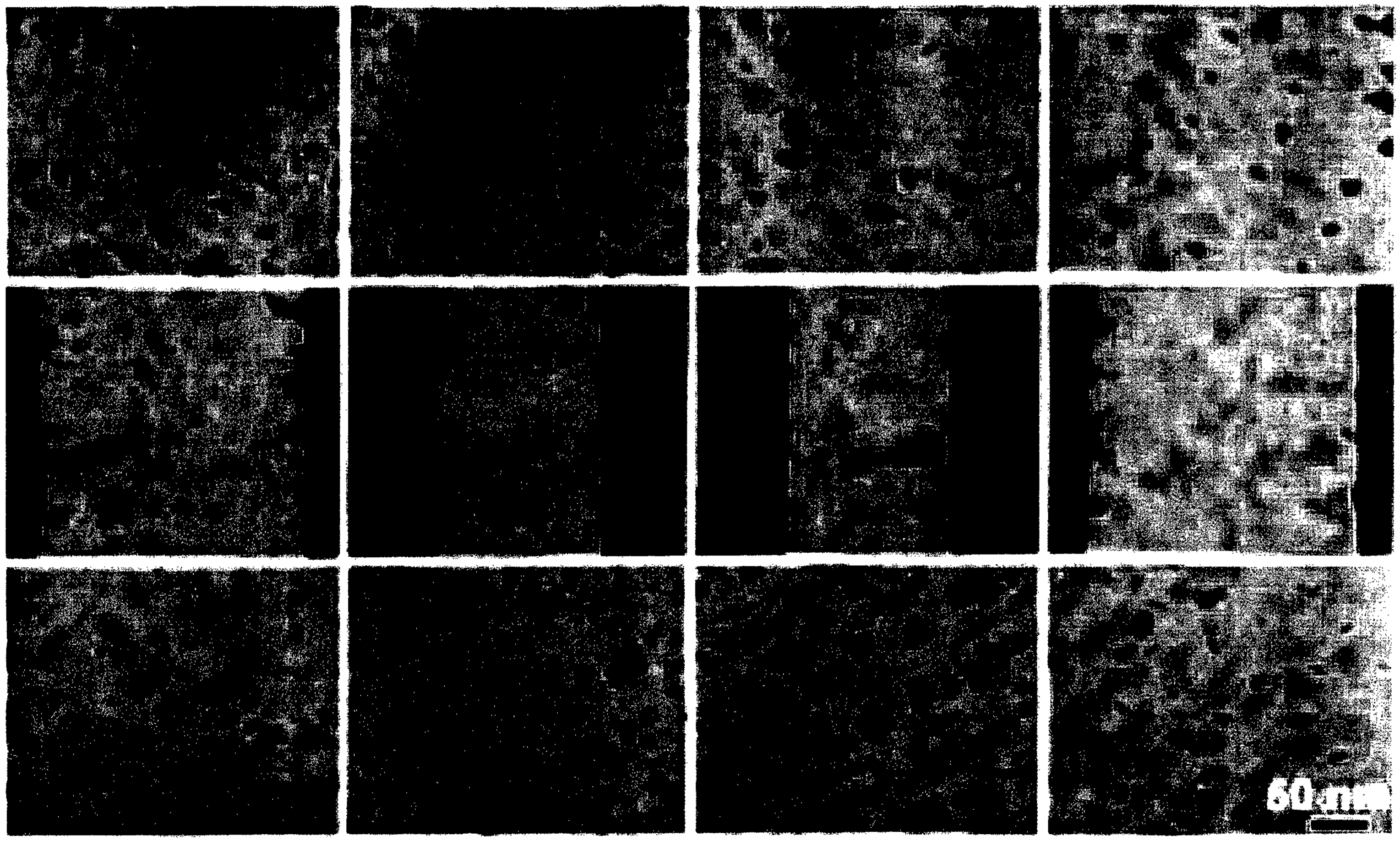


Tomograph of cylinder phase of copolymer blend; 10° rotations.
Spontak *et al.*, *Macromol.* **29** (1996) 4496



Tomograph of gyroid phase of copolymer blend; 20° rotations.
Spontak *et al.*, *Macromol.* **29** (1996) 4496

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Microphase Separation

- ***Repulsion between incompatible polymer segments***

$$\varepsilon_{ij} = -\sum \frac{3}{4} \frac{I_i I_j}{I_i + I_j} \frac{\alpha_i \alpha_j}{r_{ij}^6}$$

$$\chi = \frac{1}{kT}\left[\varepsilon_{AB} - \frac{1}{2}\left(\varepsilon_{AA} - \varepsilon_{BB}\right)\right]$$

- ***Condition for microphase separation: $\chi N > 10$***
  - **χN controls segregation**
  - **N_A/N_B controls phase structure**

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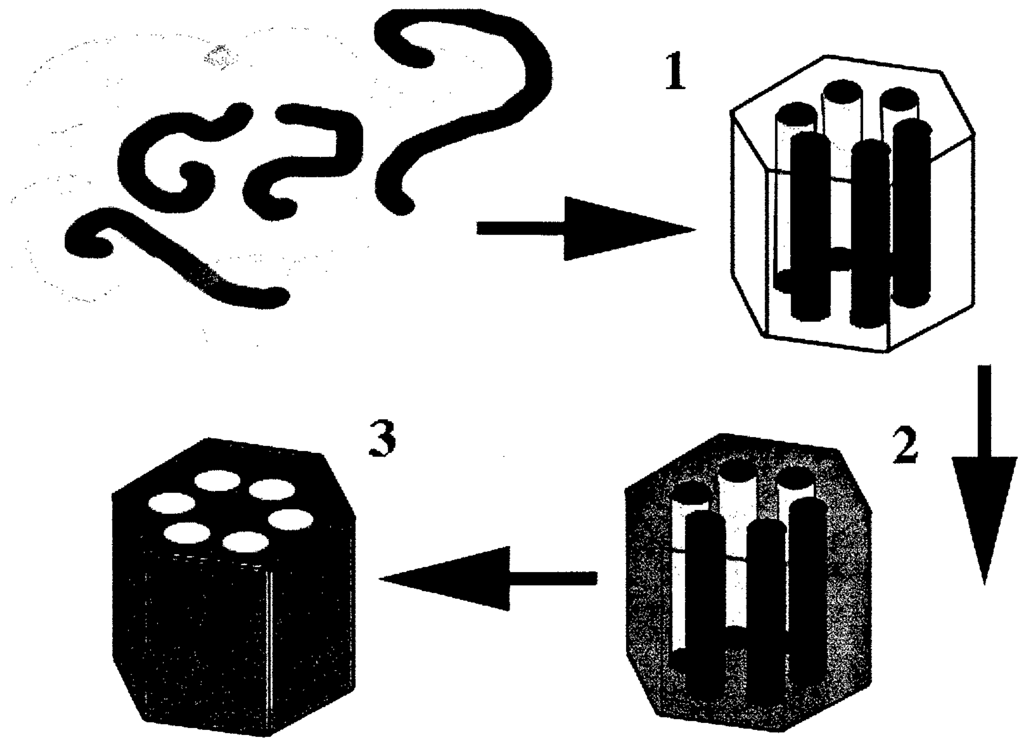
Strategy

- *Synthesize cylinder phase diblock copolymer (A:B = 1/3)*
- *Make A segment labile*
- *Cross-link B segment*
- *Cross-link, degrade and remove A, characterize by x-ray and EM*



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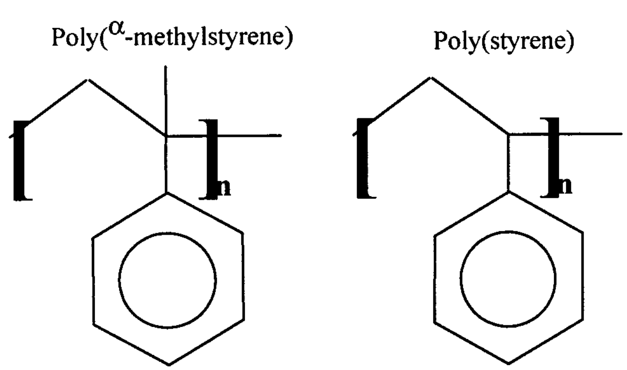
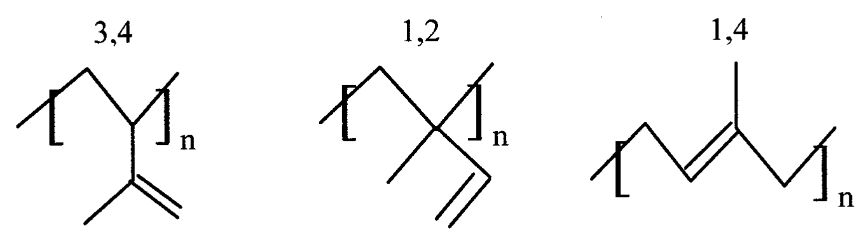
Microphase Separation

- ***Our polymer:***
  poly(α-methylstyrene)-b-poly(isoprene) diblock copolymer
  - **1:3 ratio by weight**
  - **Hexagonal (cylindrical) microstructure**





Three isomers of poly(isoprene)

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Experimental Procedure

1. *Synthesize*
2. *Solvent cast from toluene onto teflon*
3. *UV cross-link*
4. *Heat under vacuum to degrade, remove α-methyl styrene*
5. *Characterize*

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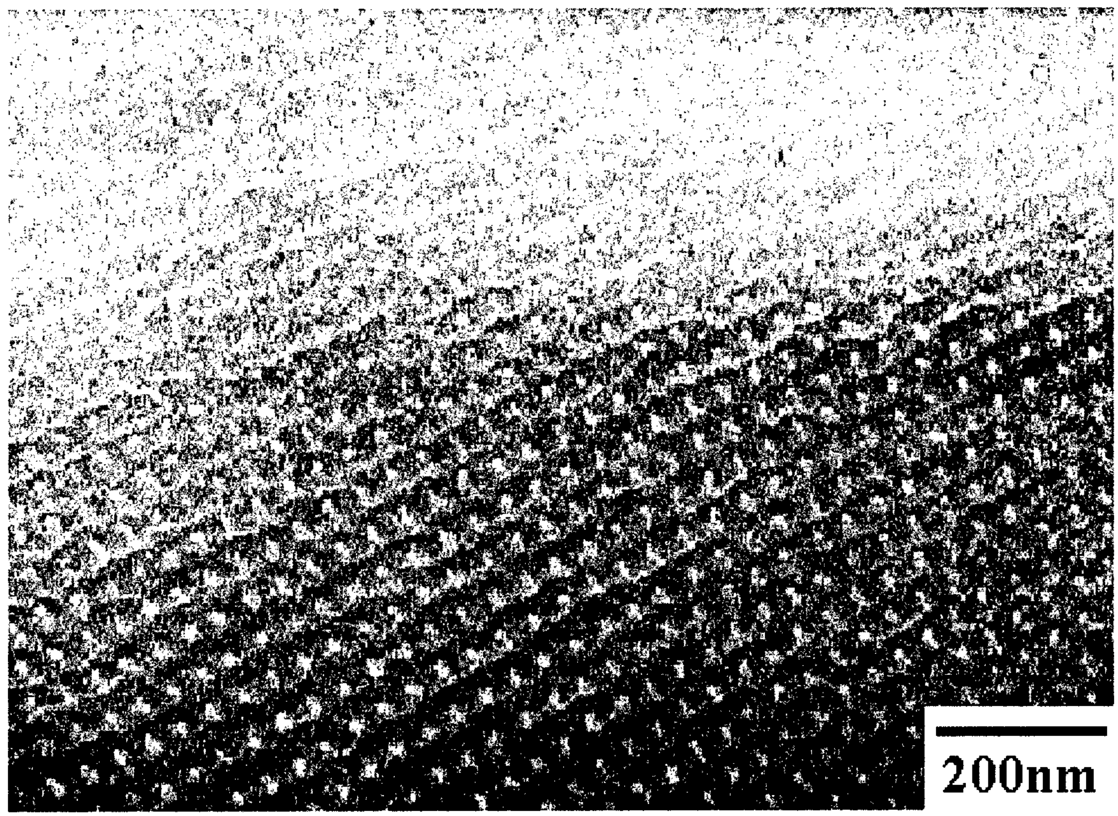
Results

- ***Microstructure visible in TEM***
  - Pores!!!



Positive image

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Next Steps

1. *Synthesize other polymers to move into bicontinuous region*

2. *Explore other polymers chemistries*

3. *Back-fill cross-linked polymer host with organic and inorganic guest molecules, for different properties*

SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

The Sponge Phase: Applications

DANIEL M. DABBS[§,#], SOL M. GRUNER[‡], KAREN J. EDLER[‡], NAN YAO[#], AARON RABINOVITCH[‡], AKIN AKINC[‡], ROBERT K. PRUD'HOMME[§,#], AND ILHAN A. AKSAY[§,#]

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FIFTH ARO/MURI PROGRAM REVIEW

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

SEPTEMBER 28 - 29, 1999

Department of Chemical Engineering and
Princeton Materials Institute
Princeton University

L_3 "Sponge" Phase: Applications

Daniel M. Dabbs,[*§] Karen J. Edler,[‡] Kate M. McGrath,[†]
Nan Yao,[§] Sol M. Gruner,[‡] and Ilhan A. Aksay[*§]

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Princeton University, Princeton, New Jersey 08540

[‡]Physics, Cornell University,
Ithaca, New York 14850

[†]Chemistry, University of Otago,
New Zealand

Supported by ARO/MURI under grant DAAH04-95-1-0102

The Sponge Phase–Applications

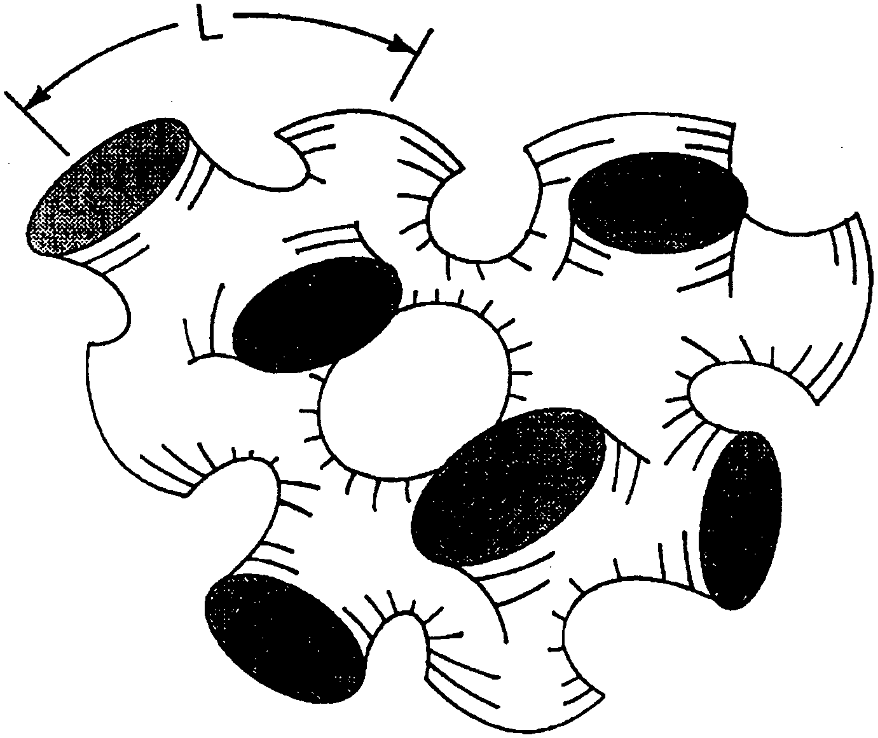
- *Objectives*
  - **Develop mesostructured cellular ceramics for use in specific applications, involving**
    - monoliths for matrix support
    - coatings and thin films
- *Approaches*
  - **Retention of mesostructure during and after templation**
  - **Efficient extraction of organic component**
  - **Silicate as a passivating coating and support matrix**
  - **Eventual templating using other metalloorganic systems**

L_3-Templated Silicates

- ***Silica deposition on isotropic L_3 phase yields high surface volume with contiguous, uniform pore structure***
- ***Materials can be supercritically extracted to remove template (N. Mulders, University of Delaware) resulting in optically transparent media***
- ***Application development***
  - **Holographic storage medium (H. Katz, Lucent Technologies)*:**
    - High permeability to monomeric precursors
    - *In-situ* reaction and curing to form photoactive matrix
    - Two-photon read-and-write through transparent composite
  - **Thin films and coatings**

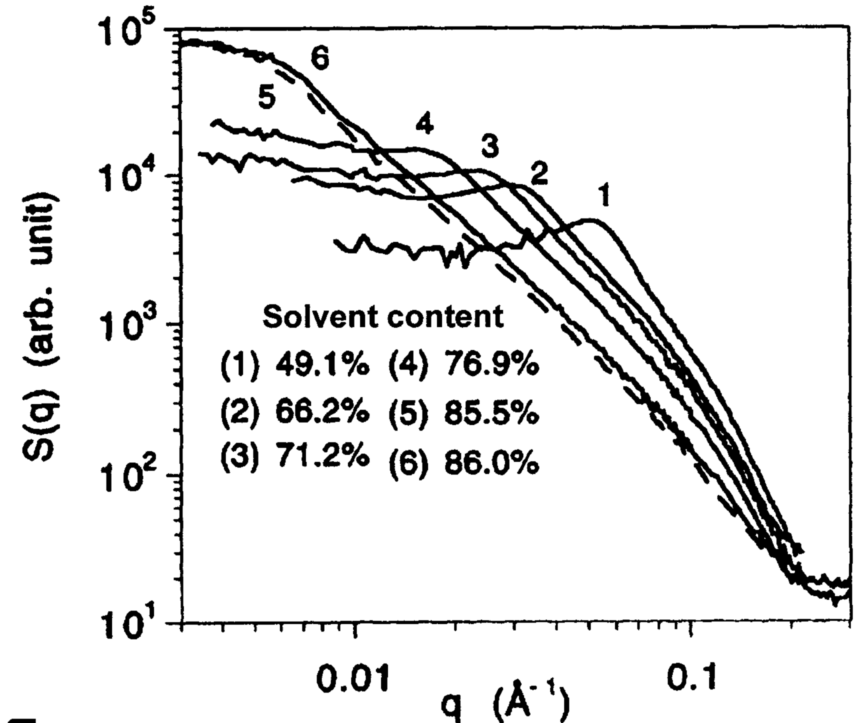
**Postdoctoral researcher support provided for two years ($100,000)*

D. M. Dabbs, S. M. Gruner, H. Katz, N. Mulders, and I. A. Aksay



G. Porte *et al.*, *J. Phys. (France)* **49** (1988)

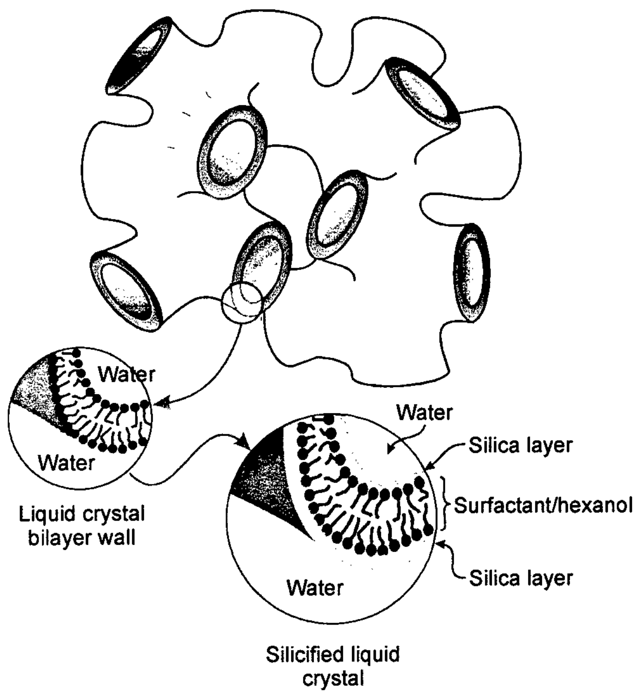
$$L = \frac{2\pi}{q_c}$$

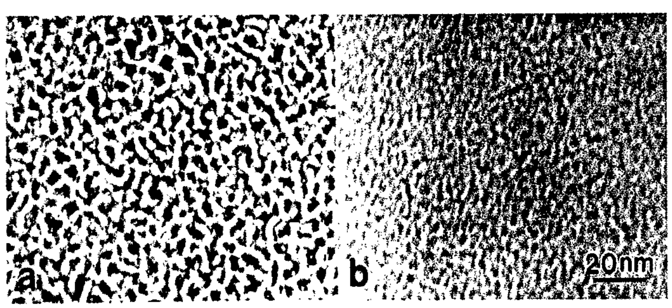


Lei *et al.*, *Phys. Rev. E* **56** [1] (1997)

- ***Flexible, sponge-like liquid crystal composed of surfactant bilayers separating primary volume into 2 bicontinuous volumes***
- ***5 nm - 1 μm cell lengths (L) inversely related to q vector ($q = 4\pi\sin\theta/1.54$ Å)***
- ***"Dilution effect:" increasing solvent content expands cell length***

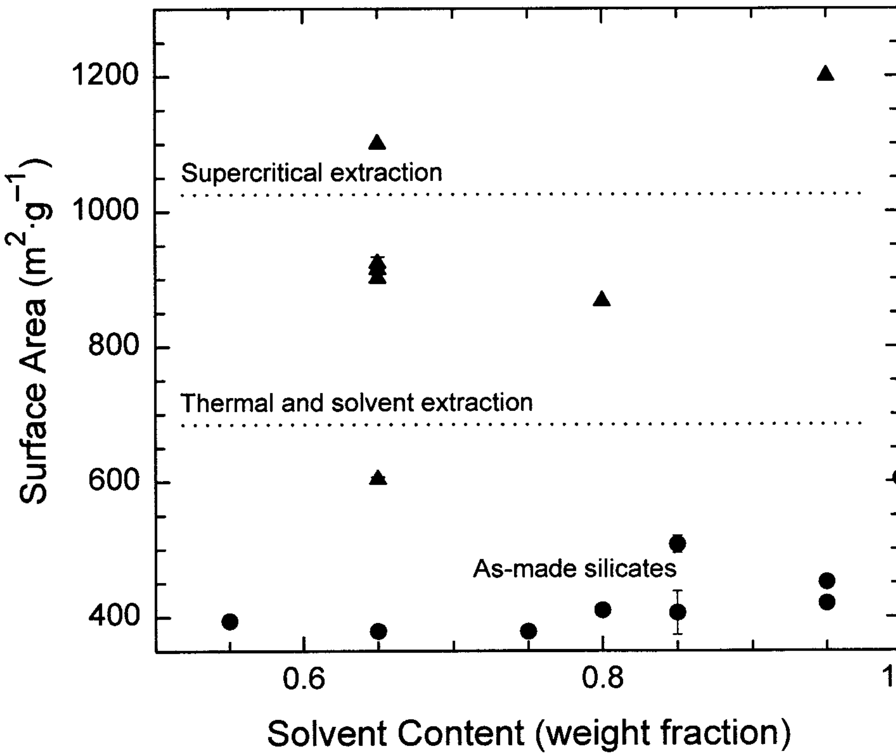
Past Studies





L_3 silicate, dried

Silica xerogel



K. M. McGrath, D. M. Dabbs, N. Yao, I. A. Aksay, and S. M. Gruner, *Science* **277** 552-6 (1997)

K. M. Mcgrath, D. M. Dabbs, K. J. Edler, N. Yao, I. A. Aksay, and S. M. Gruner, *Langmuir* (in press, 1999)

K. M. McGrath, D. M. Dabbs, I. A. Aksay, S. M. Gruner, U.S. Provisional Patent Application Serial#60/047,463; Docket No. 97-1407-1 (1997)

Comparative Properties of SCE-L_3 Silicates

- ***SCE-L_3 Silicates***
  - Density:
    ~0.25 g/cm^3
  - Surface Area:
    400-1200 m^2/g
  - Pore size:
    narrow distribution,
    controlled diameter
    (5 nm to 100 nm)

- ***Aerogels***
  - Density:
    0.7-0.001 g/cm^3
  - Surface Area:
    400-1000 m^2/g
  - Pore size distribution:
    <2nm "micropores",
    2-50nm "mesopores",
    >50 nm "macropores"

Applications

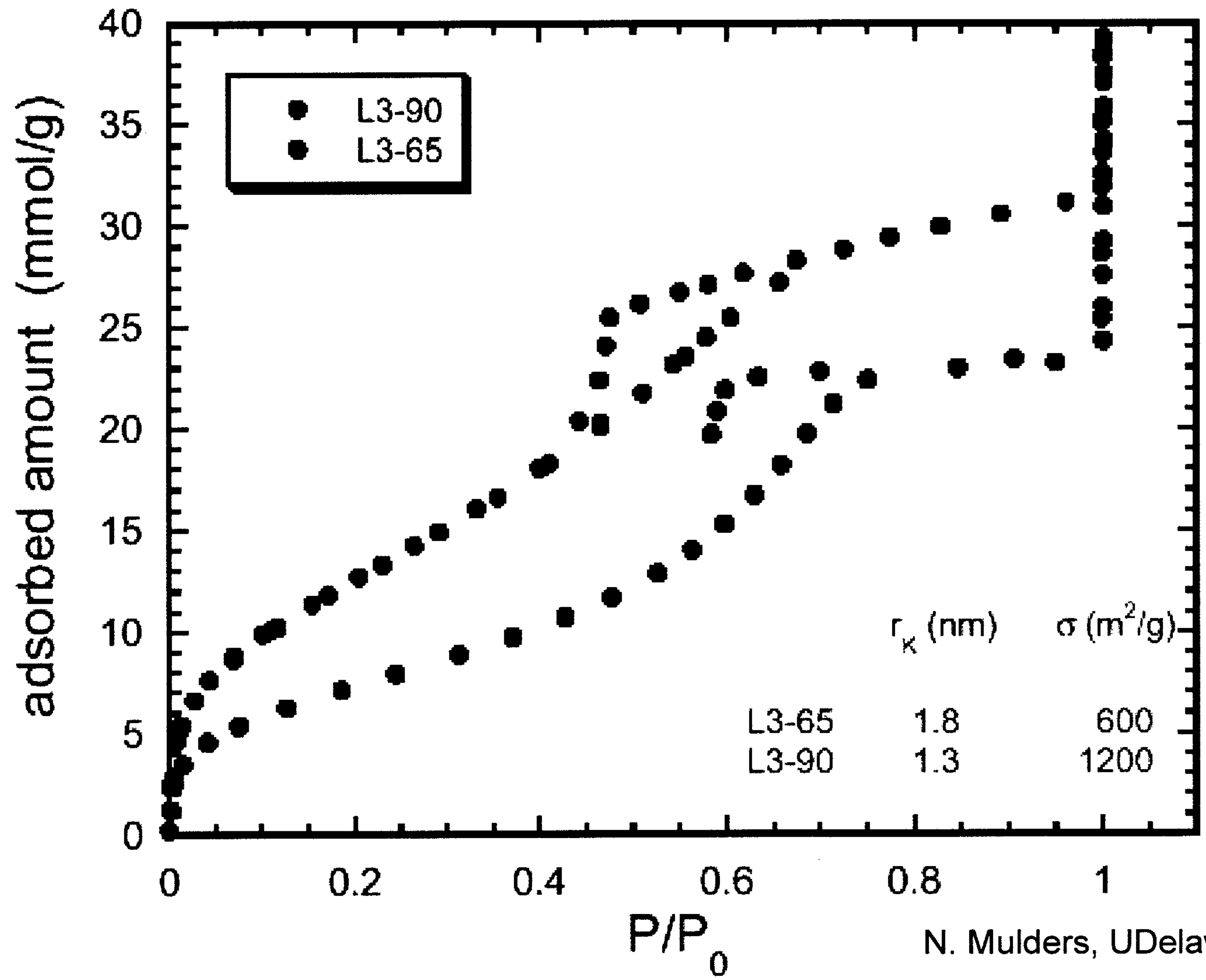
- *Current studies*
  - Low index optical material
  - Ultracapacitors
  - Heavy metal and pollutant scrubbers
  - Thin films and monoliths for sensors and optoelectronics
  - Catalysts and catalyst supports
- *Potential applications*
  - Selective liquid barriers
  - Osmotic membranes
  - Energy storage
  - Controlled filtration
  - Insulation
  - Nanocomposites
  - Encapsulation of proteins and macromolecules

Applications of the L_3 Phase: Current Studies

- ***Supercritical Extraction***
- ***Monoliths***
  - **Composite structures**
    - Cellular matrix composites
  - **Holographic imaging (Lucent Technologies)**
  - **Ultracapacitors**
    - Metallization via electroless deposition
- ***Thin films***
  - **Passivating layers (low *k* dielectric materials)**
    - PZT microcantilevers
  - **Active sensors**

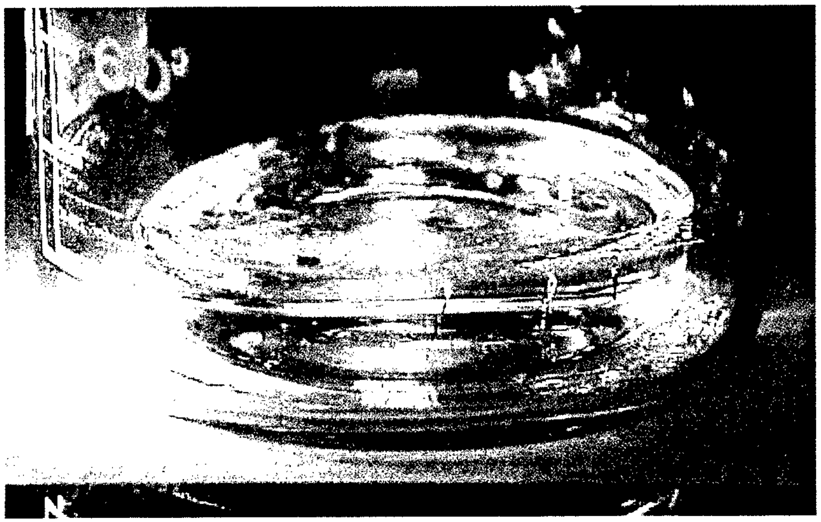
Supercritical Extraction

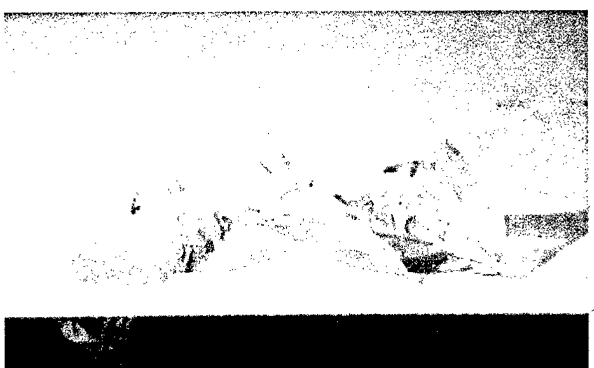
230°C, 130 bar
(methanol)



N. Mulders, UDelaware

Monoliths

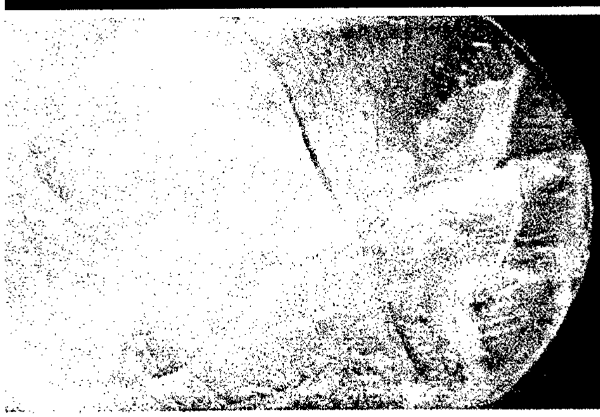


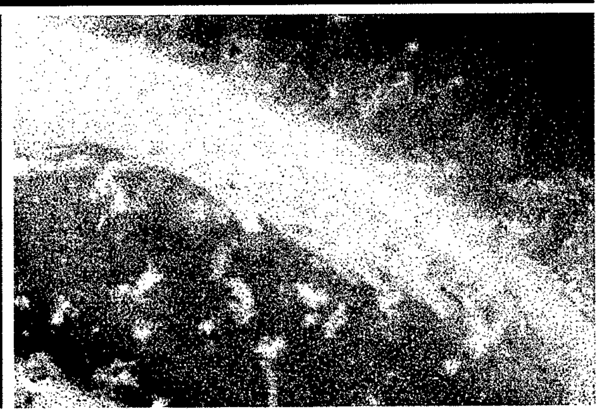


- *As cast, slow dried in sealed container*
  - Shrinkage up to 20-30% (by volume)
  - Low strength
  - Highly sensitive to air
  - Very long processing times (>3 months)
- *Supercritical extraction*
  - N. Mulders, UDelaware
  - Shrinkage <5% (by volume)
  - Mechanically robust

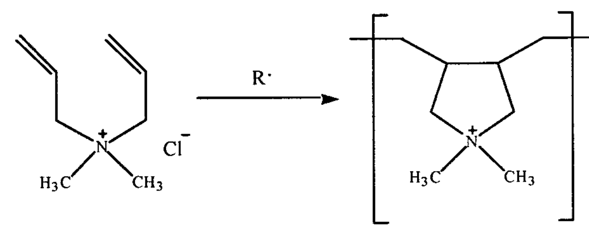
Permeability of Matrix: A Simple Polymer/Silicate Composite:

composite | silicate + monomer | composite | composite





In situ polymerization



K. J. Edler, and S. M. Gruner, unpublished research (1998)

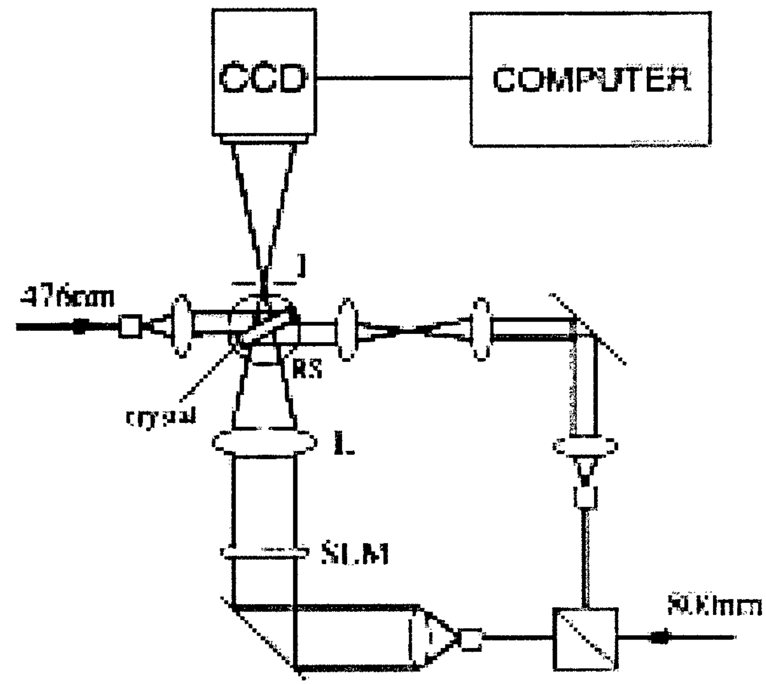
Holographic Storage Medium

- ***Store information 3-dimensionally, throughout the medium, not 2-dimensionally as with other storage technologies***
  - Collaboration with H. Katz, Lucent Technologies*
- ***Uses few or no moving parts, permitting greater data processing speeds***
- ***High storage densities***
- ***Parallel data read for faster access***
- ***Robustness and error insensitive (e.g., redundant)***

**Postdoctoral researcher support provided for two years ($100,000)*

Nonvolatile Volume Storage

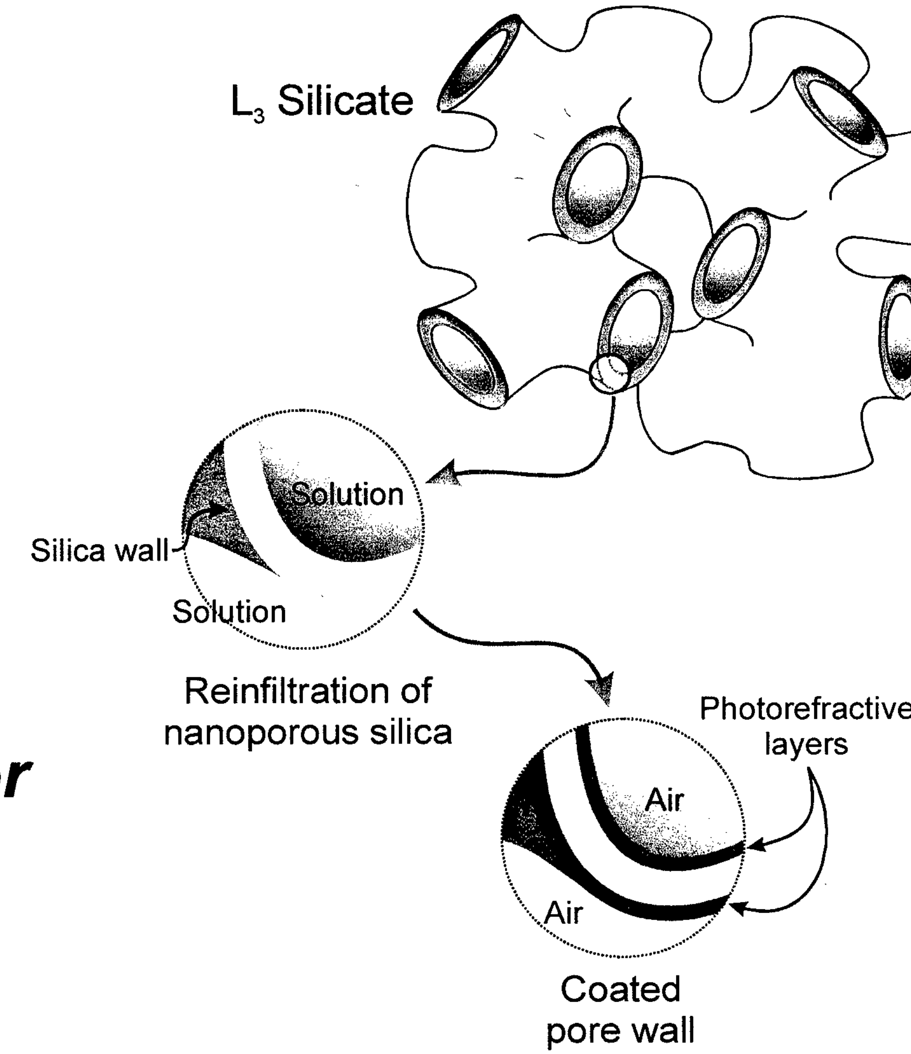
- ***Write function superposes two wavelengths***
- ***Read function uses one wavelength, preventing data erasure during read***
- ***Efficiency of storage medium affected by:***
  - Scattering from matrix
  - Photosensitivity during read/write
  - "Cross-talk" at high information densities



L. Hesselink, S. S. Orlov, A. Liu, A. Akella, D. Lande, R. R. Neurgaonkar, *Science* **282** 1089-94 (1998)

L_3 Silicate as Support Matrix

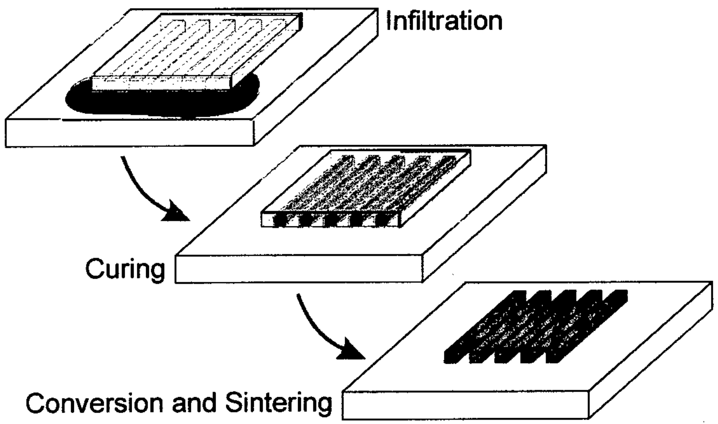
- ***Infiltration of matrix with precursor solutions***
  - Lucent Technologies
- **In situ *reaction to form photorefractive material***
- ***Large pore diameters (>400nm) to maintain transparency***
- ***High density cell walls for improved durability***
- ***Low cost***



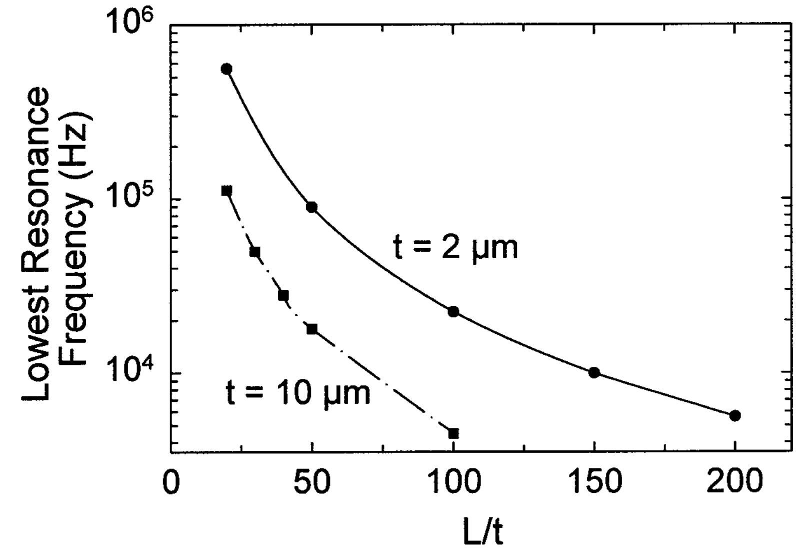
Thin Films and Coatings

- ***Coatings in micro-electromechanical systems (MEMS)***
  - **Combining MEMS-based sensors with biological receptors**
    - Collaboration with J. Carbeck, Princeton University
    - *In vivo* microdevices for biosensing applications
  - **Role of the mesostructured silicate:**
    - Help to chemically passivate PZT to retard leaching
    - Protect and isolate metallic electrodes from the environment
    - Provide a surface for the coupling of receptors and ligands
- ***Thin films***
  - **Continuous films for low *k* dielectric applications**
    - High uniform porosity with structural coherence

PZT Microcantilever

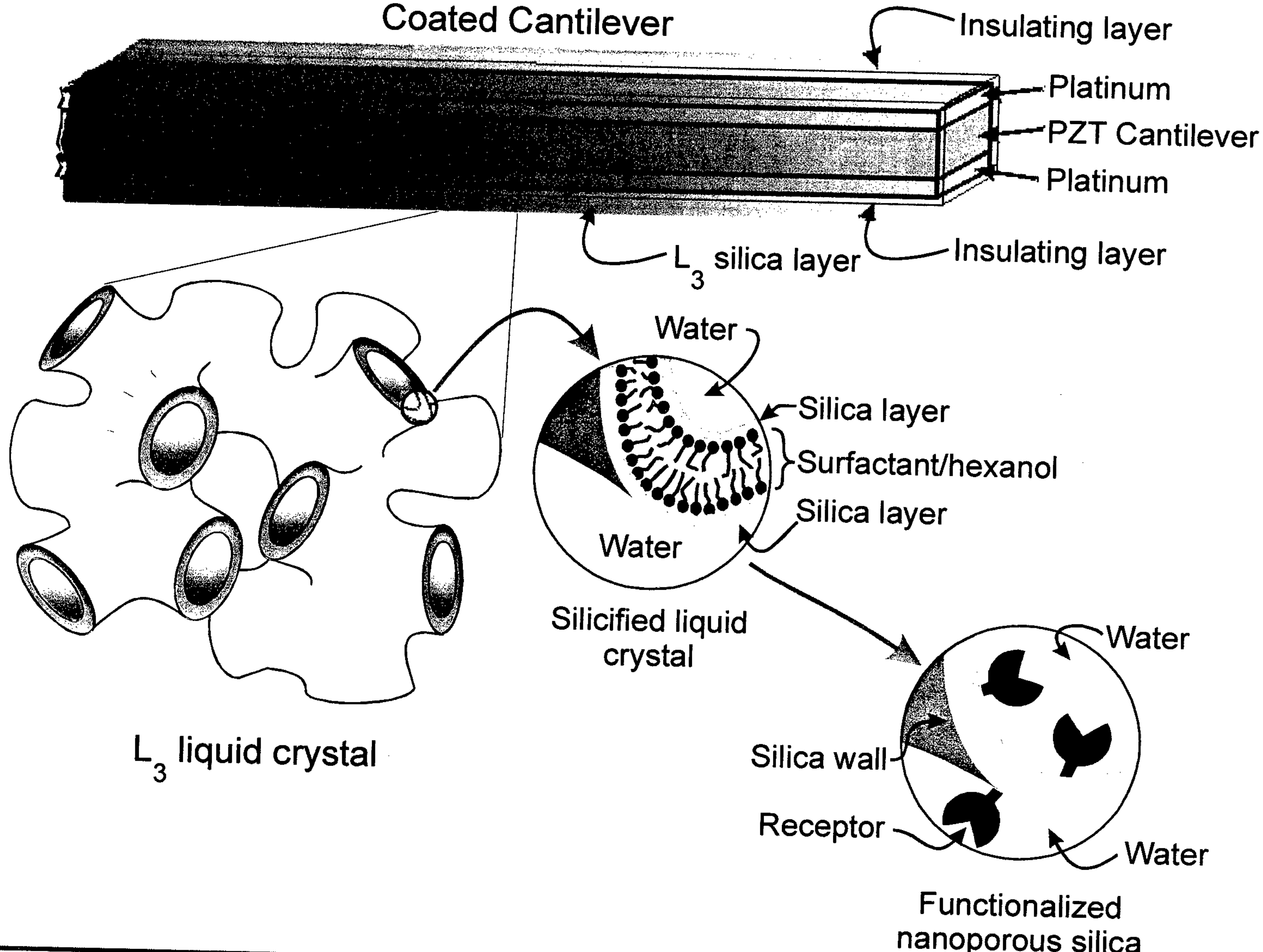


Micromolding

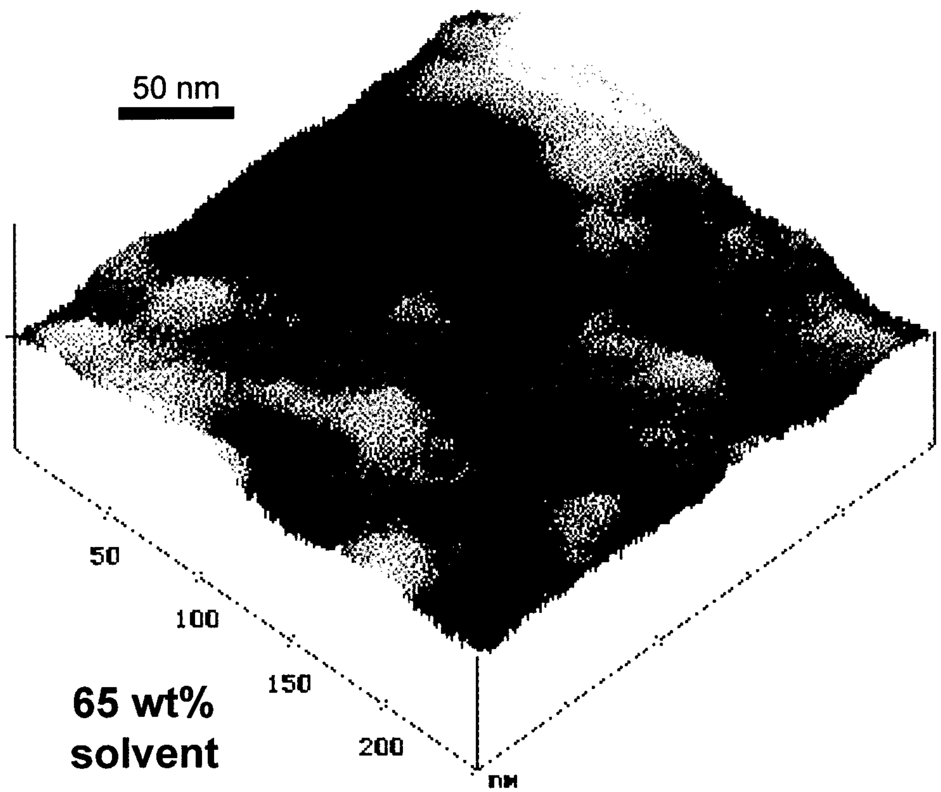


Calculated frequency response

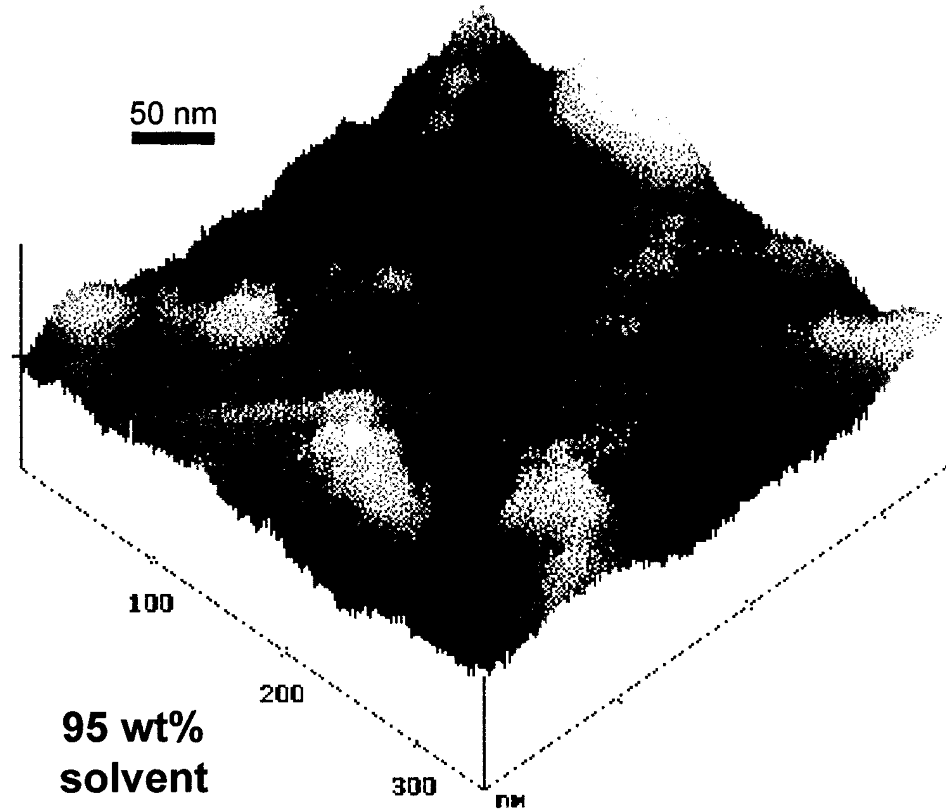
Mesostructured Coating on PZT Cantilever



Thin Films: Tunable Mesopores



65 wt%
solvent



95 wt%
solvent

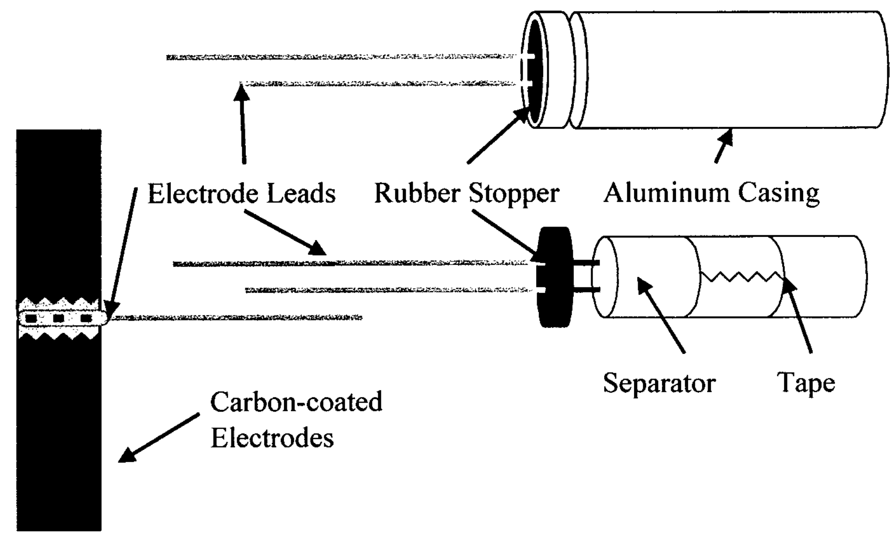
- Spin-coating retains apparent L_3 structure with tunable mesopores

Ultracapacitors

- *Goals*
  - High energy storage densities
  - Mechanically robust
- *Perceived advantages of L_3-structured materials*
  - High surface area
  - Uniform pore diameters
  - Excellent connectivity of surfaces
  - Uniform wall thickness

Commercial Ultracapacitors

- ***Approach***
  - **Determine necessary conditions for ultracapacitor through**
    - reverse engineering of commercial ultracapacitor
    - constructing a comparable ultracapacitor from high surface area materials and appropriate electrolyte
  - **Utilize L_3-templated substrates for constructing ultracapacitor**



Schematic of a Panasonic Gold series ultracapacitor (EECA0EL334); a high surface area carbon-coated electrode is formed into a spiral wrapping around a central electrode lead; high conductance electrolyte fills the voids

Cyclic Voltametry for Measuring Capacitance

$$\text{Capacitance} = \frac{1}{2}\oint I dV \left[\frac{dV}{dt} V_P\right]^{-1}$$

where:

closed loop is the "voltage window"

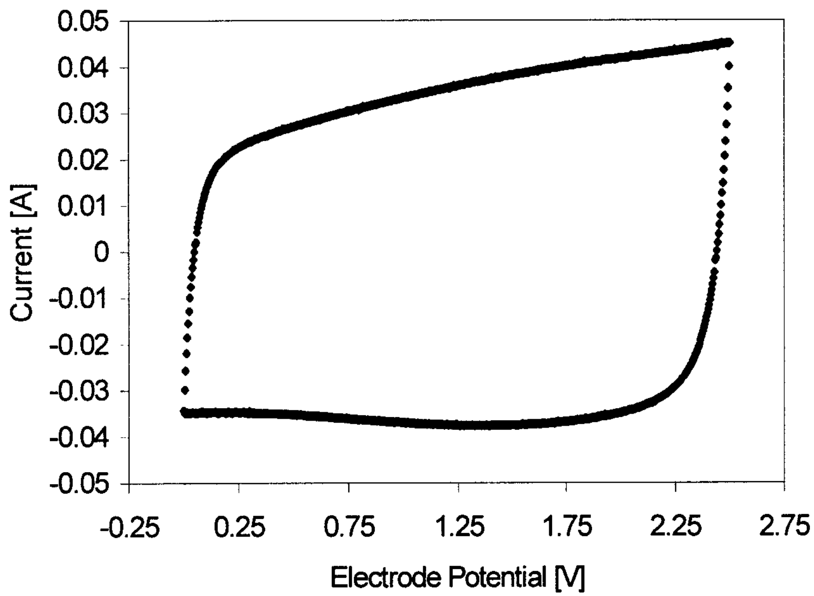
I *is the current in amperes*

V *is the electrode potential in volts*

dV/dt *is the voltage sweep rate in* $V\ s^{-1}$

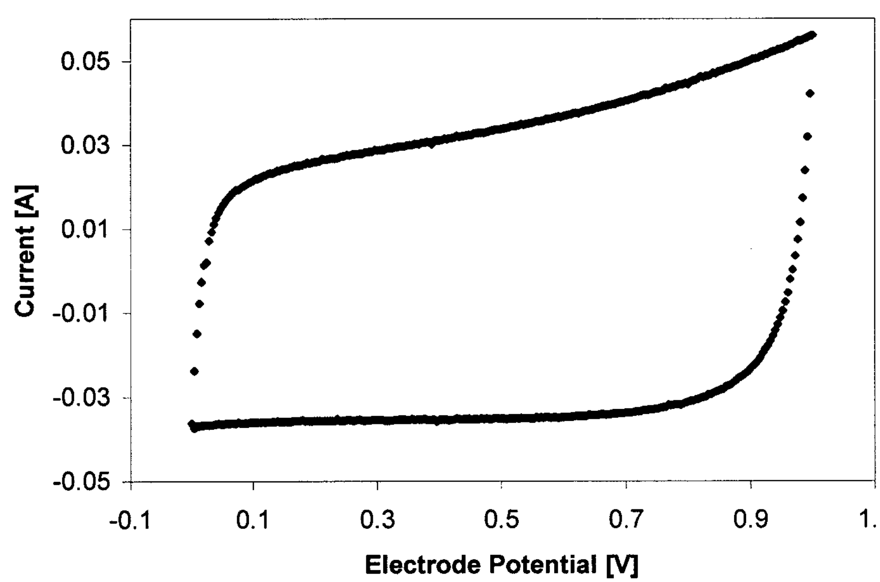
V_P *is the peak voltage*

Comparison of Commercial and Model Ultracapacitors



Panasonic EECA0EL334 ultracapacitor
Capacitance = 0.33 F

Specific surface area = 1040 ± 20 m^2g^{-1}



LLNL carbon model ultracapacitor
Capacitance = 0.33 F

Specific surface area = 700-750 m^2g^{-1}

Results and Future Work

- *Highly conductive substrate coupled with high surface area are mutual requirements for ultracapacitance, based on enhancing the double-layer*
- *L_3 silica must be activated for use in ultracapacitors*
  - Possible activation of surface by electroless deposition of metal on pore walls
- *L_3 structured, high conductivity substrates through direct templating of liquid crystal*

Continuing Studies

- *Ultracapacitors*
  - Direct templation of liquid crystal
  - Metallization of pore walls through electroless deposition
- *Holographic Media*
  - Casting of suitable monoliths
  - Supercritical extraction
  - Reinfiltration and *in situ* processing of photorefractive layers on mesostructured silicate substrate
- *Thin Films and Coatings*
  - Passivating layers
  - Activated surfaces (biosensors, metallization)